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On the Bands at λ 2536 and λ 2540 of Mercury

By

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ABSTRACT.

Two bands at λλ 2536 and 2540 which are generally accepted as responsible for the molecules of mercury (Hg_2) have been investigated under various physical conditions.

1. The ordinary non-luminous vapor of mercury shows a strong absorption band at λ 2536 shaded towards the red and a very much weaker one at λ 2540 shaded in the opposite direction.

2. The luminous vapor, which is isolated from the negative arc of mercury in the air with a small horse-shoe magnet, shows the strong bands at λ 2540 and λ 2536 in absorption and the band at λ 2536 in emission.

3. The luminous vapor highly excited in the positive column of a vacuum tube emits the band at λ 2540 without the noticeable band at λ 2536.

It is concluded that the band at λ 2536 might be of the arc type, responsible for the neutral moleclue (Hg_2), and the band at λ 2540 might be of the spark type and responsible for the ionized one (Hg_2^+).

The band spectra of mercury were first studied by Wood and Guthrie[1] and subsequently by Stark and Wendt,[2] McLennan and Edwards,[3] Nagaoka,[4] and many other investigators.

In the band spectrum of mercury two different types of bands are easily noticed. The bands of the first kind are generally located in the less refrangible part of the spectrum the strongest of which are of wavelengths 4219, 4017 and 3728. At a moderate dispersion the component

1 Astro. J., **29**, 211 (1909).
2 Phys. Zeits., **14**, 562, 567 (1910).
3 Phil. Mag., **30**, 695 (1915).
4 Jap. J. Phys., **1**, 1 (1922—24).

lines of these bands are fairly resolved. Series of investigations have been recently carried out upon these bands by Compton and others[1,2,3,4,5] with the conclusion that the carriers of these bands might probably be ascribed to the excited mercury hydrides (H_gH). Quite recently Hulthén[6] has analysed the same bands and came also to the conclusion that the emitters of this band spectrum must be molecules composed of a mercury atom and atoms of an element of low atomic weight, since the wide spacing of the band lines indicates a small moment of inertia of the molecule.

In the second kind of bands, on the other hand, the bands at λ 2536, λ 2540 and also these located at the more refrangible part of the spectrum, all with apparently unresolvable structures might be included.

Now, the possibility of the existence of the diatomic mercury molecule Hg_2 has been suggested by Frank and Grotrian.[7] The expected value of the order of the magnitude of the distance between the successive band lines is but 10^{-3} A for the green light, and it is thought quite appropriate to ascribe the apparently continuous bands of the second kind to the diatomic molecule Hg_2. Tate's[8] recent experiment has also shown that the band at λ 2540 might be responsible for the molecule Hg_2.

In the course of an investigation upon the arc spectrum of mercury in the air the present writer has found a remarkablly strong development of an absorption band at λ 2540 as well as the band at λ 2536 near the mercury cathode of a vertical arc, the anode being a coreless carbon rod. On sending the current in the reverse direction in this vertical arc, these bands practically disappeared, a strong reversal of the resonance line over the entire length of the arc only remaining. In the present paper these two bands at $\lambda\lambda$ 2536 and 2540 have been examined under different excitations and various physical conditions, and some discussions have been offered under the hypothesis that both bands are responsible for the diatomic mercury molecules.

Results.

A coreless carbon rod of 1 cm. in diameter was pierced at one end. The hole was filled with mercury and this was utilized as one of the electrodes in our vertical arc, the other electrode being a coreless carbon

1 Phys. Rev., **23**, 768 (1924).
2 Phys. Rev., **24**, 597 (1924).
3 Phil. Mag., **48**, 898 (1924).
4 Phys. Rev., **25**, 606 (1925).
5 Phil. Mag., **49**, 360 (1925).
6 Zeits. f. Phys., **32**, 110 (1925).
7 Zeits, f. Phys., **4**, 89 (1921).
8 Phys. Rev., **25**, 110 (1925).

of the same size. The applied voltage was varied from 110 to 440V and the current was regulated from 2 to 5 A with high resistance nickel-chrome wires arranged in series.

A small and a medium quatz Hilger spectrographs were used and the image of the arc was focussed upon the slits of these spectrographs with a quartz fluorite achromatic combination.

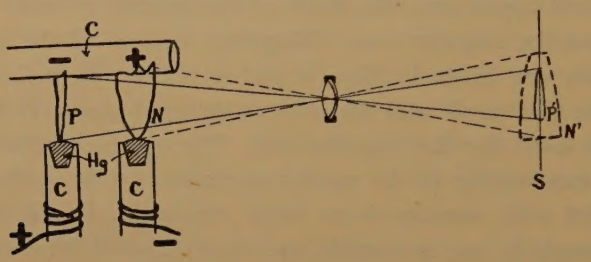
In general appearance, the form of the positive mercury arc is quite different from the negative one. Magnified images of the positive and negative arcs are given in Eigs. 1 and 2, Pl. I. In both arcs the applied voltage was 220V and the current traversed was 3·1A for the positive arc and 2·6A for the negative one. The positive arc is quite stable, but in this case owing to the rapid vaporization of the mercury, the cup must be filled with mercury at an every exposure. In the negative arc, however, though the arc is unstable, the vaporization of the mercury is fairly small, and the arc can be maintained without charging the mercury to secure several photographs.

For the spectroscopic examination of these arcs an entire image of the arc was focussed upon the slit of the spectrograph, and the distribution of the spectral lines over the whole length of the arc was examined. With a mercury anode and a carbon cathode the lines due to mercury are generally strong near the mercury electrode, and gradually lose their intensities as they proceed towards the cathode. Though the spark lines such as at λ 2848 and λ 2248 are faint, they however show their appearances extended further up to the carbon electrodes. Besides this, the reversal of the resonance line is remarkable. Next, with a mercury cathode and a carbon anode the line distribution in its spectrum is almost the same as that of the former one. The spark lines mentioned above are, however, strong at the cathode surface showing a larger concentration of the ionized mercury atoms in this region than at the anode surface of mercury. In addition to this, I found a remarkable development of the dark bands at λλ 2536 and 2540 in the spectrum of the light from the neighbourhood of the cathode surface where the spark lines are emitted most strongly. These bands are utterly absent in the spectrum of the positive arc. This is clearly visible in the photographs given in Figs. 3 and 4, Pl. I, and also in the enlarged ones (Figs. 5 and 6, Pl. I).

The continuous background due to the broadening of the line at λ 2536 emitted at the central core of the arc was absorbed at λ 2536 and λ 2540 by the luminous outer layer near the cathode surface of the arc. The development of the band at λ 2540 is quite remarkable, its intensity being nearly equal to that of the band at λ 2536.

Next, a fine image P′ of the positive arc P(source) was formed upon the slit S of our spectrograph through the luminous vapor layer of the negative arc N(absorber), N′ being the out-focussed image of the negative arc N as indicated in the following diagram (Fig. 1) and the absorption of the latter arc was examined.

Fig. 1.



The continuous background due to the broadening of λ 2536 in the spectrum of the former (positive arc) was absorbed at $\lambda\lambda$ 2540 and 2536 by the latter (negative arc) as may be seen in the spectrum given in Fig. 8, Pl. I, the upper one (Fig. 7, Pl. I) being that of the source alone. With a positive arc absorber no such absorption bands were obtained.

The luminous vapor capable of producing the absorption band at λ 2540 has an ionized character, and this is easily deflected or isolated from the arc in any desired direction with a small horse-shoe magnet. If we deflect the luminous excited vapor towards the slit or along the line of sight (i. e. increasing the thickness of the absorbing layer), the development of the absorption band at λ 2540 is remarkablly strong, its intensity being several times stronger than that at λ 2536. Next, if we deflect the excited vapor outside the line of sight no trace of the band at λ 2540 is obtained in the spectrum. The spectrum of this isolatable luminous vapor was taken and it was found that in this spectrum there was no trace of the band at λ 2540 observed in emission nor in absorption, and the band at λ 2536, on the other hand, appeared as an emission, being sharply defined at wave-legth shortor side and shaded towards the red. This is shown in Fig. 11, Pl. I, the upper ones (Figs. 9 and 10, Pl. I) of this spectrum are those of the light from a quartz mercury lamp. The lower is the spectrum under the weak, and the upper under the heavy, current excitations, showing the symmetrical broadening of the line at λ 2536.

On a closer examination upon the light of the positive arc of mercury a fainter bluish fluorescent light has been observed just above the boiling mercury anode with a comparatively non-luminous space about 0·5 mm. thick between. The intensity of this fluorescent glow becomes tolerably

stronger as it proceeds towards the luminous arc. This is seen in the photogragh of the positive arc (Fig. 1, Pl. I), but a greater part of the image of this luminous glow is disappeared in this reproduction, a trace at the right side of the arc and near to the mercury surface only remaining. In the spectrum of this fluorescent glow, as already been observed by wood and others, the resonance line λ 2536 is predominant, and in addition we have a band in the extreme violet and another band in the green, the latter accounting for the visible luminousity of the fluorescence.

The vapor was next excited in a vacuum tube by an induction coil of a medium size. At a certain vapor pressure the vapor came to emit the band at λ 2540 only with no noticeable trace of the band at λ 2536. One of the photographs thus obtained is given in Fig. 13, Pl. I and a

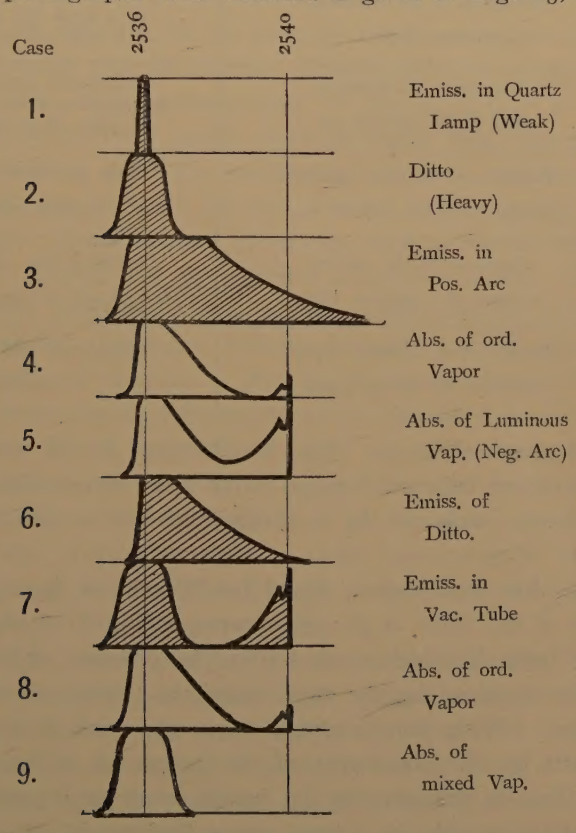


Fig. 2.

negative arc spectrum is also given in the upper one for comparison sake.

The diagrammatical representation of the intensity curves of these bands obtained in the spectra under various conditions are also given in

Table I.

Case	Discription of Source and Absorber in Fig. 2.	Analysis.
1	Emission in quartz lamp under weak current excitation.	Sharp line at λ 2536 in emission.
2	Ditto under heavy current excitation.	Broadening of the line at λ 2536 in emission.
3	Emission of the positive arc in the air.	Broadened line and band shaded towards the red at λ 2536 both in emission.
4 and 8	Absorption of non-luminous ordinary vapour.	Broadened line and band at λ 2536 and weak band at λ 2540 all in absorption,
5	Absorption of luminous vapor in the cathode arc.	Broadened line and band at λ 2536 and storong band at λ 2540 all in absorption.
6	Emission of luminous vapour isotated from the cathode arc.	Line and band at λ 2536 both in emission.
7	Emission in the positive column of a vacuum tube.	Broadened line at λ 2536 and strong band at λ 2540 in emission.
9	Absorption of ordinary vapor mixed with foreign gases.	Broadened line at λ 2536 in absorption.

the annexed sketch (Fig. 2). The manifoldness in the modifications of the spectral region between λ 2536 and λ 2540 is remarkable. This is, however, plainly explained by a simple hypothsis as given in the above table.

The peculiar modification, found by Wood,[1] in the appearance and the position of the band at λ 2536 (corresponding to 8 and 9 in Fig. 2 and also in Table I.) which resulted from the presence of the foreign gas, is completely explained by the above view, the reason of which might be as follows: — With pure mercury vapor the excited atoms which are brought forth by the absorption of the resonance radiation will partly re-emit the line on returning to the normal state and partly combine in their excited states with the normal atoms forming the diatomic molecules Hg_2 which show the characteristic asymmetrical absorption band shaded towards the red. With an admixture, on the other hand, though the

1 Astro. J., **27**, 41 (1907).

activated atoms are also produced at the expense of the resonance radiation, they will combine with the mixed gas molecules and therefore the band at λ 2536, responsible for the diatomic molecules of mercury, practically disappear, the strong reversal of the resonance line alone remaining.

The present experiment indicate that the more heavier the vapor is excited the more strongly the band at λ 2540 is enhanced. With normal non-luminous vapor the absorption band at λ 2536 is prevailing and only a trace of the band at λ 2540 appears. Next, with excited luminous vapor which is positively charged and produced at the cathode surface, both absorption bands come out in nearly equal intensities. Lastly, on the degree of excitation being still further raised, the vapor is caused to emit the band at λ 2540 without the sensible band at λ 2536.

Now, in the negative arc of mercury, large numbers of the ionized atoms are produced near the mercury cathode which is readily seen to be the case by the strong enhancement of the spark lines in this region. These ionized atoms will partly emit the spark lines, and then the arc lines in combination with the neighboring electrons, and partly combine in their ionized state with the normal mercury atoms forming the ionized molecules Hg_2^+. These ionized molecules thus produced will show, on being animated further, the characteristic absorption bands. Besides these ionized molecules, there might exist in the excited luminous mercury vapor numbers of excited molecules without ionization as was already conjectured by Frank and Grotrian.[1] Among the bands corresponding to the two kinds of molecules in different states of activity, it is quite natural to consider that the former bands (spark type) should become pronounced as the vapor is excited more heavily in comparison with the latter ones (arc type) as is the case with the spark and arc lines in atomic radiation. From this point of view it might be quite appropriate to conclude that the band at λ 2540 is responsible for the ionized molecules Hg_2^+ and the band at λ 2536 for the neutral molecules Hg_2.

Steubing[2] has already observed an electrical conductivity of the mercury vapor illuminated by ultra-violet lights such as a spark or a mercury lamp, showing that the vapor is ionized by the ultra-violet lights. Moreover, it was found in the present experiment that the band at λ 2540 was remarkablly developed in the positively charged vapor in absorption. These two facts will be quite in harmony with our conclusion that the band at λ 2540 might be one of the spark bands of the mercury molecules.

Again, it may be imagined that the main constituents of the posi

1 Loc. cit.

2 Phys. Zeits., **10**, 787 (1909).

tively charged vapour, freshly liberated from the negative arc and deflected by the magnet, might be ionized molecules at an energy level ready for the band absorption at λ 2540 in their ionized states, and for the band emission at λ 2536 on catching the neighbouring electrons and returning to their neutral state.

Lastly, the possible reason for the absence of the band at λ 2540 in the positive arc might be the too small concentration of the ionized molecules to produce the sensible absorption owing to the rapid diffusion of these ionized molecules towards the cathode by the action of the electric force acting between the electrodes of this arc.

In conclusion, the writer wiches to express his hearty thanks to Prof. M. Kimura, who gave valuable advice in the present investigation and took much interest there-in

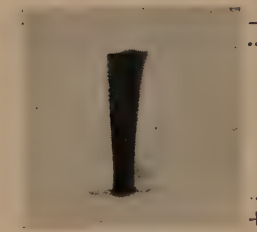
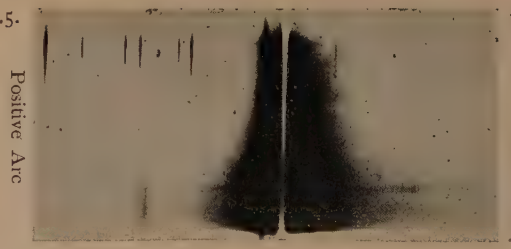
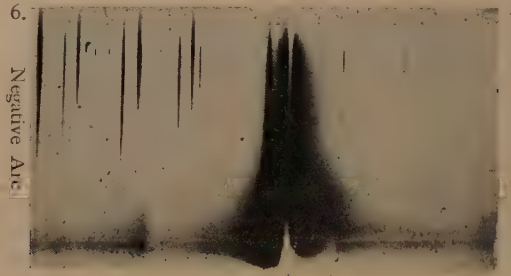
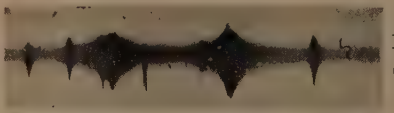


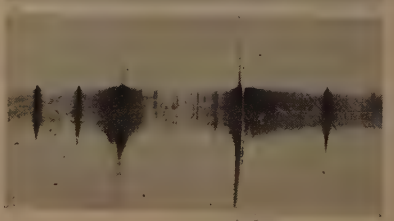
Fig. 1. Positive Arc

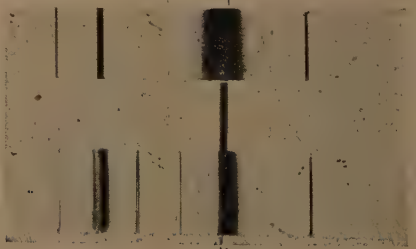
Fig. 2. Negative Arc











Excitation of Enhanced Lines of Tin in Arcs and Zeeman Effect of Certain Enhanced Lines of Tin.

By

Michika Miyanishi.

(Received November 30, 1925)

ABSTRACT

Excitation of the enhanced lines of tin in arcs: —
The enhaced lines of tin have already been classified by Kimura and Nakamura into spark, super spark and super-super spark lines. In this investigation the excitation of these lines in arcs was studied, a grating spectroscope being used. The lines λλ 5800, 5590, 5563, 5333, etc. belonging to the first type were observed clearly in the light emitted from the alternating current arc and Poulsen's arc charged with metallic tin. Using Poulsen's arc without self-induction it was found that the light emitted at the instant of the break of this arc takes a spark character when the capacity shunted between the arc terminals is increased to 0·25 microfarad, and the current before the break to 7 A. In this light the lines λλ 5370, 5344, 5289, 5225, 5101, 5021, 4934, 4858, 4615, 4586 belonging to the second type were newly observed. These results will show that the excitation energy of the super spark lines is greater than that of the spark ones.

Zeeman effect of the lines λλ 5800, 5590, 5563 and 5333: —
As the light source a discharge tube containing $SnCl_3$ was used. When the light was analysed by a spectrograph containing a 20-plate echelon grating and a large direct vision prism, these lines seemed to be single lines in the zero field. When the self-induction and capacity in the discharge circuit were adjusted these lines resolved into magnetic triplets in the field of 15900 gauss. Their separations were about one third of the normal triplet.

An arc spectrum of tin, especially in the visible part of the spectrum, consists of a few lines, while its spark spectrum contains many lines. The lines enhanced in passing from arc to spark are generally called enhanced lines. Recently Kimura and Nakamura[1] classified the enhanced lines of tin into spark, super spark and super-super spark ones. In the

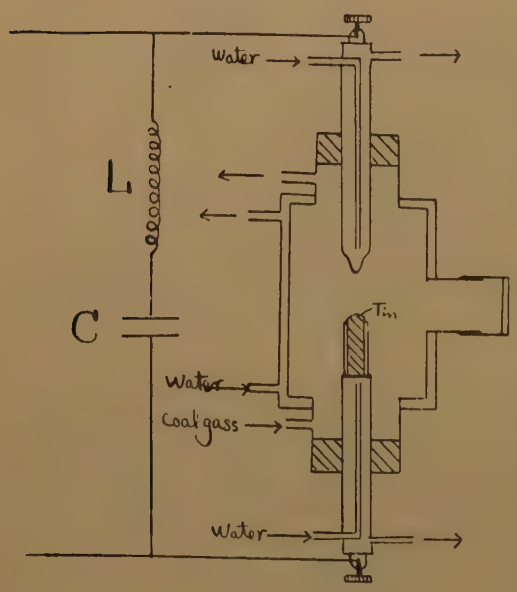
1 Jap. J. Phys., **3**, 29 (1923).

present experiment an effort was made to see how such lines can be excited in lights emitted from various sources. As sources of light, the alternating current arc, Poulsen's arc employed in the production of undamped electric oscillations, and the light emitted at the instant when a circuit was broken, were used.

(1) Alternating Current Arc: A vertical arc was started between carbon electrodes by 440-volt A.C. circuit through a proper resistance. A small hole was made in the lower carbon and was charged with a piece of metallic tin. The image of the light from such an arc was projected on the slit of a spectrograph having a good replica grating for the dispersing system, and the spectrum was photographed with a camera provided with a photographic lens of 50 cm. focus. The spectrum thus taken showed that the enhanced lines $\lambda\lambda$ 6453, 5800, 5589, 5563 and 5333 are emitted in the neighbourhood of the lower electrode containing the metal. These lines are, according to Kimura and Nakamura, the spark lines of tin emitted by a singly ionized atom of the element. In the same spectral region the spark spectrum contains such lines as $\lambda\lambda$ 5370, 5344,....., but they could not be detected in the present arc.

(2) Poulsen's Arc: Next, the light emitted from Poulsen's arc was studied. The arrangement for obtaining the arc is shown in the accompanying figure. The upper electrode consists of a water cooled copper tube provided with a copper cup and the lower one the carbon rod perforated with a small hole containing a piece of tin. Such electrodes were placed in a water-cooled chamber having a glass window, coal gas being circulated through it. A large condenser of the capacity of about 0·3 microfarad and a suitable coil were connected in series with the arc terminals and the arc was started by 440-volt D.C. circuit. The light emitted from this arc was studied by the above grating spectrograph. The spectrum

Fig. 1



thus obtained is represented in Fig. 3 which shows both arc and spark lines.

The enhanced lines observed in the spectrum are λλ 6453, 5800, 5589, 5563, 5333, etc. which according to the above investigators are the lines of Sn^{+}, no lines of Sn^{++} being observed. By reducing the self-induction and increasing the capacity of the condenser, spark lines got intensified at the expence of the arc lines, but no super spark lines made their appearance yet.

(3) The light emitted at the instant of the break of a 440-volt D.C. circuit: The self-induction in the Poulsen's arc was taken out from the circuit, and the upper electrode was first brought into contact with the lower tin electrode, and then quickly separated from it. The spectrum of the light thus emitted consisted of arc and spark lines. The capacity shunted between the arc terminals was gradually increased from 0·02 to 0·3 microfarad, and the current flowing in the circuit when both electrodes were in contact was also increased from 5 to 8 amperes. This increase of both the current and the capacity gave the light a spark character, reducing the intensity of the arc lines and augmenting that of the spark lines. The enhanced lines λλ 5370, 5344, 5289, 5225, 5101, 5021, 4934, 4858, 4615, 4586 were newly observed when the capacity reached the value of about 0·25 microfarad, and the current of 7 amperes. These lines were intensified as the capacity of the condenser was increased. They are lines of the super spark spectrum of tin. Thus, the spark and then super spark lines were excited in this light when the capacity was gradually increased and the above group of enhanced lines consequently required greater energy for their exciation than those of the former group of the enhanced lines. The order of the appearance of such enhanced lines leads to the same conclusion as that obtained by Kimura and Nakamura.

Lastly the influence of the presence of such electronegative gases as bromine, chlorine and iodine on the spectrum of the light emitted by an electric arc in it was studied. The result of the experiment will be given in a separate paper.

Zeeman Effect of the lines λλ 5800, 5590, 5563 and 5333.

The Zeeman effect of the lines of tin has been studied by Purvis[1]. The greater part of the lines studied by him being arc lines, and a few, enhanced ones. It is very desirable to examine the Zeeman pattern of

1 Proc. Camb. Phil. Soc., **13**, 82 (1906).
〃 〃 〃 〃 **14**, 217 (1908).
Phys. Zeits., **8**, 594 (1907).

more enhanced lines. In the present experiment, the tube containing $SnCl_3$ excited by an induction coil giving 15 cm. spark in air was used as the light source. The form of the discharge tube is shown in Fig. 2, the internal diameter of the capillary being about 3 mm. L representing a coil of various self-induction, and C the condenser of the capacity of about 0·001 microfarad. As the spectroscopic instrument a 20-plate

Fig. 2

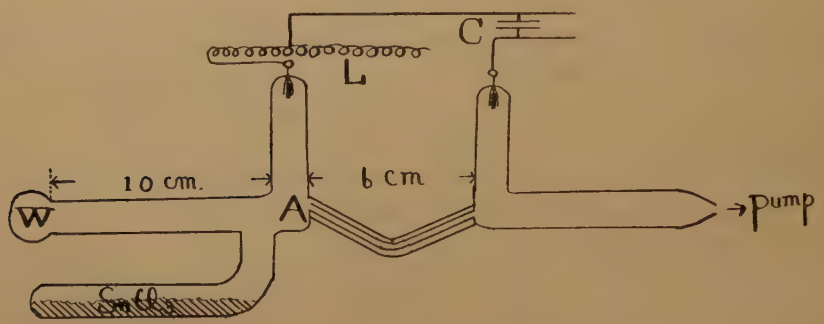


Table.

λ	Δλ	Nature of the polarization	$\frac{\Delta\lambda}{\lambda^2 H}\times 10^1$	$\frac{\lambda\Delta}{\lambda^2 H}\Big/0{\cdot}94\times 104$
5800	+0·18	s.	0·34	0·36
	0·00	p.		
	−0·17	s.	0·32	0·33
5590	+0·17	s.	0·34	0·36
	0·00	p.		
	−0·17	s.	0·34	0·36
5563	+0·16	s.	0·33	0·35
	0·00	p.		
	−0·17	s.	0·35	0·37
5533	+0·15	s.	0·33	0·35
	0·00	p.		
	−0·15	s.	0·33	0·35

echelon grating combined with a large direct vision prism was used. This echelon is the same one as used by Hori[1] in his study of the structure of bromine lines and its constant was fully described in his paper. The part A of the capillary was placed between a pair of truncated pole pieces of an electromagnet of the Du Bois type, the diameter of the end of the pole piece being 7 mm., and they were set at a distance of

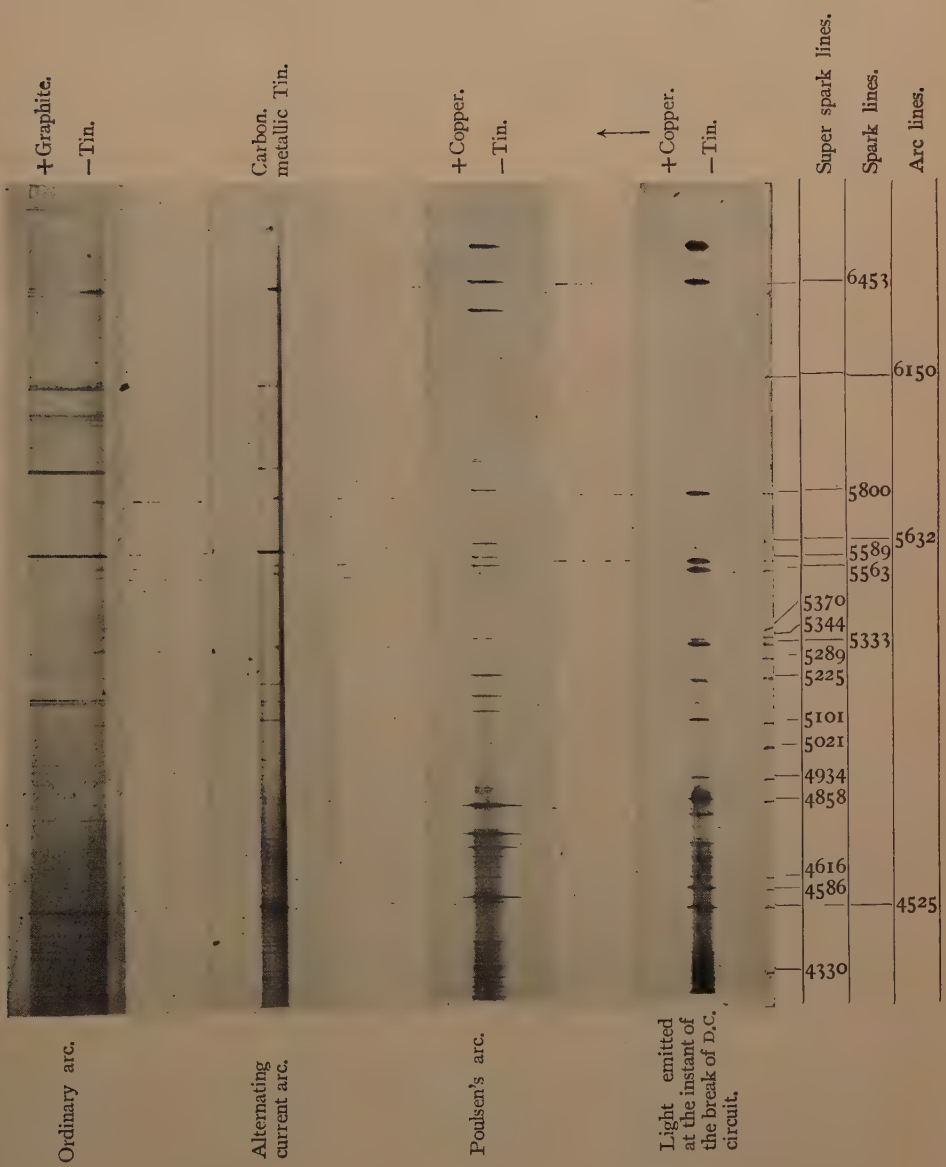
1 These Memoirs, **9**, 307 (1926).

7 mm. apart. The light emitted from the part A of the tube through the window W was analysed by the above echelon spectroscope. The lines $\lambda\lambda$ 5800, 5590, 5563 and 5333. seemed to be single lines in the zero field, but they were resolved into magnetic triplets in the magnetic field, though they were not sharp. Proper adjustment of the self-induction and the capacity in the discharge circuit made the lines sharper and their magnetic separation in the field of 15900 gauss could be photographed with an exposure of about 6 hours. The polarization was studied by means of a calcite plate.

The results obtained are given in the table. Thus, these lines were resolved into magnetic triplets, but their separations were about one third of these normal triplets.

In conclusion, the writer wishes to express his best thanks to Prof. M. Kimura under whose guidance the present experiments were carried out.

Fig. 3.


+Graphite.
−Tin.
Carbon.
metallic Tin.
+Copper.
−Tin.
+Copper.
−Tin.
Super spark lines.
Spark lines.
Arc lines.
6453
6150
5800
5632
5589
5563
5370
5344
5333
5289
5225
5101
5021
4934
4858
4616
4586
4525
4330
Ordinary arc.
Alternating current arc.
Poulsen's arc.
Light emitted at the instant of the break of D.C. circuit.

Large Displacements of the Spectral Lines of Chlorine.

By

Kwan-ichi Asagoe.

(Received November 30, 1925)

In the course of an investigation of the spectrum of chlorine to classify the lines into arc and spark types, certain lines were found to suffer large displacements when the methods of the excitation were varied. This peculiar phenomenon attracted my interest, and the behaviour of lines in the region from λ 5457 to λ 2577 was investigated.

The study was carried out with the following two spectrographs:—

1. A five-prism spectrograph. This was constructed with five 60° glass prisms made by Hilger (length of the base 64 mm.), and an achromatic camera lens of 53 cm. focus. All the optical system of the instrument was placed in a wooden box, temperature of the enclosure being kept constant to within 0·1° C by an alcohol thermostat. This spectrograph was used to study the lines lying between λ 4585 and λ 3833, the dispersion on the photographic plate being about 0·085 mm. per 1 Å at λ 4570 and 0·266 mm. at λ 3833.

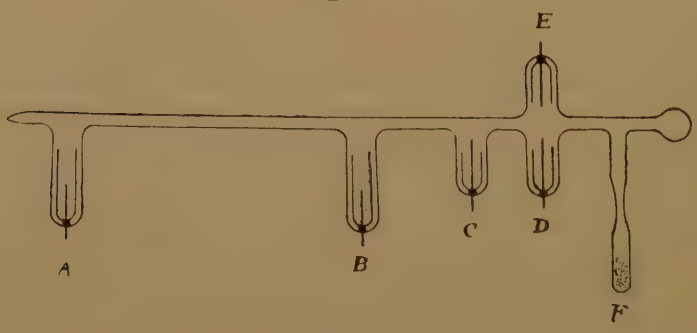
2. A concave grating of three meter focus. This was employed in the region from λ 5457 to λ 4585 and from λ 3833 to the ultra-violet, spectrograms being taken in the first order, and the dispersion was constant (0·181 mm. per 1 Å.) in the whole region investigated.

The vacuum tube used in this experiment was constructed in the following way:— A certain quantity of well-dried sodium chloride was put in a small glass cup having a platinum wire sealed in one end, and this was again sealed in an outer tube. Two tubes of such construction were connected to a main tube of about 3 mm. diameter, and 30 cm. in length, one end of which was blown out into a fine bulb. Besides these, another side tube containing a small quantity of well-dried cupric chloride

was connected to the main discharge tube. During the evacuation of the tube, the glass walls were well heated, and a condensed electric discharge was sent through. After this treatment, the side tube containing the cupric chloride was properly heated and chlorine gas was driven out, and this was again evacuated to a suitable pressure. The tube was then sealed off from the pump when the discharge became bright. The tube thus prepared was excited by an electric discharge from a condenser of the capacity of about 0·008 μF charged by a 20 cm. induction coil. The image of an end-on emission from the tube was projected by an achromatic lens on the slit of the spectrograph, and the spectrum was photographed.

Next, a pair of carbon electrodes were seated in a suitable tube of fussed quartz filled with the chlorine gas at the pressure of one atmosphere, and the spark between the electrodes was produced in the gas by the discharge from the same condenser charged by a Thorderson transformer of 3/4 kVA. giving 10,000 volts in the secondary. The spectrum of this spark was also photographed on one plate just below that of the Geissler tube. The plate thus obtained is reproduced in Fig. 1, (a) representing spectrum of Geissler discharge and (b) that of spark. Thus, it is observed that lines $\lambda\lambda$ 4573, 4570, 4277, 4271, 4254, 4241, 4236, 4234, etc. in the latter spectrum shift towards the red side as compared with the corresponding ones in the former.

Fig. 2.



It was also found that successive stages of these displcements were obtained when the pressure of the gas in the tube was varied gradually. The form of the tube employed is shown in Fig. 2. To the part of AB of the tube descrived above, another tube CDEF was connected, the distances between the electrodes B and C, C and D and D and E being 8, 2 and 0·4 cm. respectively, and the tube F containing a small quantity of cupric chloride.

First, the tube was well evacuated and an end-on emission from the tube produced by an electric discharge between A and B was photographed. Next, chlorine gas was so driven out by heating the cupric chloride that an electric discharge between B and C became very bright, and the light was photographed. This process was repeated, the pressure of the chlorine gas being increased step by step, and the spectra of the discharges between B and C, C and D and D and E were photographed one above the other on one plate. In these discharges, the condenser was charged by the 20 cm. induction coil, but it is obvious that the current desities were not the same. The plate thus obtained is reproduced in Fig. 3, in which I and V are due to the A-B discharge, and II, III and IV to the B-C, C-D and D-E discharge respectively. Unfortunately the pressures corresponding to each discharge were not measured, but the pressure in which V was taken was nearly of one atmosphere, because when the tube was broken in a pail of water after the experiment has finished, only a small quantity of water entered the tube.

The displacements of the lines in the spectrum of the spark were determined in comparison to the corresponding lines in the spectrum of the Geissler tube, the wave-lengths of the latter were taken from the tables given by Eder and Valenta[1] and Jevons[2]. In this measurement, the cross wires of a traveling microscope were set at the supposed centre of gravity of the line. But great difficulty was experienced in determining the centres of gravity on account of the diffuseness of the lines. Hence high accuracy of the readings could not be expected. The shifts from the non-shifted lines thus determined are given in Tables I, II and III.

Table I. Lines of the First Type—Arc Lines.

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder-Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
4661·38	0·35	—0·09	1·28	c	...
24·23	0·36	...	...	b	...
01·19	0·33	—0·12	1·63	a	...
4526·44	0·50	—0·09	1·65	a	...
4491·25	0·32	...	...	b	...
75·498	0·53	—0·21	1·04	c	...
69·569	0·40	...	...	c	...
46·096	0·38	...	...	c	...
38·735	0·30	...	...	c	...
03·610	0·34	...	...	c	...

1 Kayser, Handbuch der Spektroscopie. **5**, p. 307.
2 Proc. Roy. Soc., **103**, 193 (1923).

Table I. Lines of the First Type—Arc Lines. (Continued.)

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder-Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
4390·566	0·33	...	...	b	...
89·949	...	...	...	b	...
87·730	0·28 (?)	...	...	...	...
80·075	0·36	...	...	b	...
69·676	0·32	...	...	b	...
63·475	0·37	...	...	b	...
23·523	0·35	—0·15	1·26	c	...
4280·615	...	...	...	...	...
64·740	...	...	...	c	...
26·580	0·36	...	...	c	...
09·866	0·23 (?)	...	...	...	...

Table II. Lines of the Second Type—Spark Lines.

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder-Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
5457·28	0·48*	...	...	a	...
56·391	0·46*	...	...	a	...
44·412	0·50*	...	...	a	...
43·587	0·48*	...	...	a	...
23·441	0·50*	—0·36	1·68	a	...
5392·300	0·13	...	...	b	...
5285·8	0·15	...	...	...	...
21·48	0·17	...	...	b	...
18·07	0·18	—0·44	1·44	a	...
5113·3	0·15	...	...	...	...
03·18	0·14	...	...	b	...
5099·36	0·15	...	...	...	...
78·361	0·18	...	...	a	...
4995·7	0·36*	...	...	...	...
70·3	0·38*	...	...	...	...
27·3	0·41*	...	...	...	...
24·90	0·42*	...	...	...	...
17·870	0·14	...	...	b	...
04·905	0·15	...	...	a	...
4896·905	0·15	—0·65	1·82	...	...
19·628	0·15	—0·70	1·97	b	...
10·194	0·14	—1·45	3·12	b	...

Table II. Lines of the Second Type—Spark Lines. (Continued.)

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder-Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
4794·665	0·15	—1·57	3·46	b	...
85·41	0·14	...	...	...	...
81·49	0·15	...	...	c	...
79·06	0·14	...	...	c	...
71·22	0·20	...	...	...	...
68·80	0·16	...	...	c	...
55·9	0·36*	...	...	...	...
40·505	0·15	...	...	a	...
4585·05	0·29	...	...	...	...
37·0	0·67*	...	...	...	...
19·4	0·46*	...	...	...	...
04·50	0·45*	...	...	...	...
4497·45	0·66*	...	...	...	...
90·16	0·10	...	...	...	...
4399·373	0·18	...	...	b	...
73·119	0·10	...	...	b	...
43·822	0·15	—2·65	5·90	...	2
36·371	0·15	— 0·75	1·82	c	2
33·125	0·11	...	...	...	...
09·189	0·24	...	...	b	2
07·593	0·25	...	...	c	2
04·211	0·25	—0·64	1·57	c	2
4291·861	0·20	—0·68	1·50	c	2
59·628	0·27	...	...	c	2
08·160	0·20 (?)	...	...	a	...
4158·021	0·22 (?)	...	...	b	2
32·680	0·27	...	...	a	...
04·965	0·36*	...	...	...	...
3991·625	0·19	...	...	b	...
82·060	0·27	...	...	...	...
61·770	0·26	...	...	...	...
55·582	0·27	...	...	..	...
3781·378	0·34*	...	...	c	...
74·324	0·18	...	...	...	...
73·813	0·18	...	...	...	...
69·187	0·16	...	...	...	...
68·228	0·16	...	...	...	...
67·647	0·17	...	...	...	...

Table II. Lines of the Second Type—Spark Lines. (Continued.)

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder-Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
3750·102	0·16	...	...	c	...
48·594	0·17	...	...	...	...
3673·9	0·18	...	...	...	...
63·948	0·18	...	...	c	...
59·913	0·17	...	...	c	...
58·499	0·18	...	...	c	...
50·243	0·18	...	...	c	...
3353·30	0·16	...	...	c	...
33·58	0·18	...	...	...	...
29·06	0·15	...	...	b	...
20·51	0·21	...	...	...	...
16·78	0·15	...	...	...	...
15·40	0·16	...	...	b	...
07·86	0·17	...	...	b	...
06·38	0·17	...	...	b	...
3283·32	0·15	...	...	...	...
76·72	0·15	...	...	...	...
59·24	0·18	...	...	...	...
47·52	0·16	...	...	...	...
44·36	0·16	...	...	...	...
3191·40	0·17	...	...	...	...
39·28	0·16	...	...	...	...
3092·14	0·15	...	...	...	...
71·31	0·13	...	...	...	...
2965·50	0·15	..	...	...	...
2691·49	0·18	...	...	...	...
88·03	0·14	...	...	...	...
85·40	0·15	...	...	...	...
76·92	0·14	...	...	...	...
65·52	0·15	...	...	...	...
61·56	0·14	...	...	...	...
58·74	0·13	...	...	...	...
24·72	0·16	...	...	...	...
20·08	0·15	...	...	...	...
16·99	0·13	...	...	...	...
03·50	0·16	...	...	...	...
2580·69	0·14	...	...	...	...
77·13	0·16	...	...	...	...

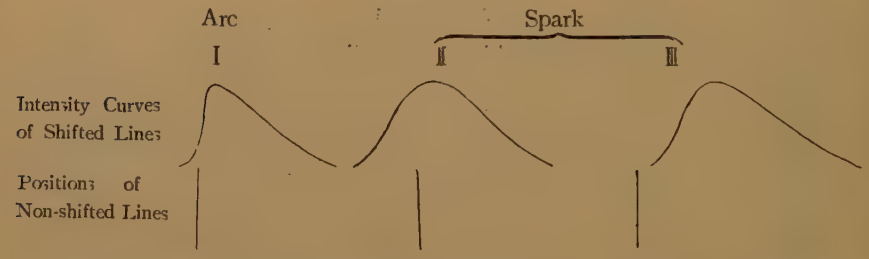
N. B. Lines marked with * suffered somewhat larger shifts than the other lines of the same type.

Table III. Lines of the Third Type—Spark Lines.

Wave-lengths of Non-shifted Lines	Shifted Lines			Eder-Valenta's Classification	Joseph Lunt's Classification
	Displacements of Centres of Gravity	Positions of Violet Edges	Breadths		
4572·79	1·81(?)	...	...	b	...
70·16	1·71(?)	...	...	...	...
4276·628	2·06	+0·53	3·37	a	1
70·725	2·10	+0·48	3·24	...	1
61·350	1·76(?)	...	...	b	1
53·532	1·85	+0·35	3·15	a	1
41·435	1·80	+0·45	3·02	a	1
35·608	1·72(?)	..	...	a	1
34·137	1·67(?)	...	...	a	1
25·139	1·93(?)	...	...	...	...
4147·203	...	...	...	a	...
24·153	0·83	...	...	...	...
3917·721	0·81	...	...	c	3
16·832	0·85	...	...	c	3
14·055	0·85	...	...	a	3
3884·045	0·88	...	...	b	3
68·844	0·89	...	...	c	3
61·008	0·88	+0·27	4·20	c	3
54·000	0·86	...	...	b	3
51·531	0·88	...	...	c	3
51·165	0·87	...	...	c	3
45·825	0·84	...	...	c	3
45·545	0·87	...	...	c	3
43·390	0·90	...	...	c	3
33·502	0·89	+0·14	2·82	a	3
29·550	...	...	...	...	...
27·802	0·89	...	...	...	3
20·404	0·88	...	...	...	3
10·215	1·14	...	...	b	...
09·697	1·11	...	...	...	3
05·384	1·12	+0·15	2·62	...	3
3725·912	0·88	...	...	...	...
3689·1	0·86	...	...	...	...
24·3	0·87	...	...	...	...
3576·211	0·83	...	...	...	...
68·08	0·87	...	...	b	...

The modes of the broadening of the affected lines may be classified into three types. The typical lines of the first type are λλ 4661, 4601, 4526, 4475, 4380, 4370, 4324, etc. All these lines are considered to be perhaps arc lines as the result of another experiment. The centres of gravity of these lines were shifted slightly to the red side. The lines are fairly sharp on the violet edge, but very diffuse on the other as shown diagrammatically by I in Fig. 4. The lines belonging to the second type are λλ 4820, 4810, 4795, 4344, 4336, 4304, 4292, 4133, etc., which are regarded as spark lines. They show no obvious displacements on mere inspection, the amount of the shifts of them being the smallest. The wings developed symmetrically on both sides as indicated in Fig. 4, II. The lines of the third type are λλ 4573, 4570, 4277, 4271, 4254, 4241, 3851, 3846, 3843, etc., and are worthy of special attention. These lines are considered to be spark lines, but they behave differently from the lines of the second type. The lines of this type lying in blue and violet were displaced about 2 Å towards the red side, while those in the ultra-violet region suffered a shift of about one half of the former. Even their violet edges are seen apparently displaced from the positions of the non-shifted lines, developing diffuser wings on the red sides as illustrated by Fig. 4, III.

Fig. 4.



Now, Eder and Valenta[1] determined the wave-lengths of chlorine lines emitted from tubes containing the gas at the pressures of 10-20 mm., 30-40 mm. and 70-100 mm. of mercury and observed the fact that, with the increase in the pressure, some of the lines became broadened especially towards the red side, some to both sides, while others remained sharp. In the above tables, such lines are indicated by a, b and c respectively. Some of them behaved similarly to ours, but many lines not.

Recently, Joseph Lunt[2] observed that certain lines of chlorine were subjected to large shifts when a condensed discharge was sent through a

1 Loc. cit.

2 Month. Not. Roy. Astronom. Soc., **85**, 148 (1924).

Geissler tube containing germanium tetrachloride or tin tetrachloride. He divided such lines into three classes. The first and second classes lie in the neighbourhood of H_γ, lines of the first showing a large displacement of about 0·8 Å, while the second only 0·1 Å. The lines belonging to the third class were found in the ultra-violet region, and suffered a shift of about 0·4 Å. In my tables, the lines thus classified by him are indicated by 1, 2 and 3 respectively. The lines of 1 and 3 are included in our Type III, and those of 2 correspond to Type II.

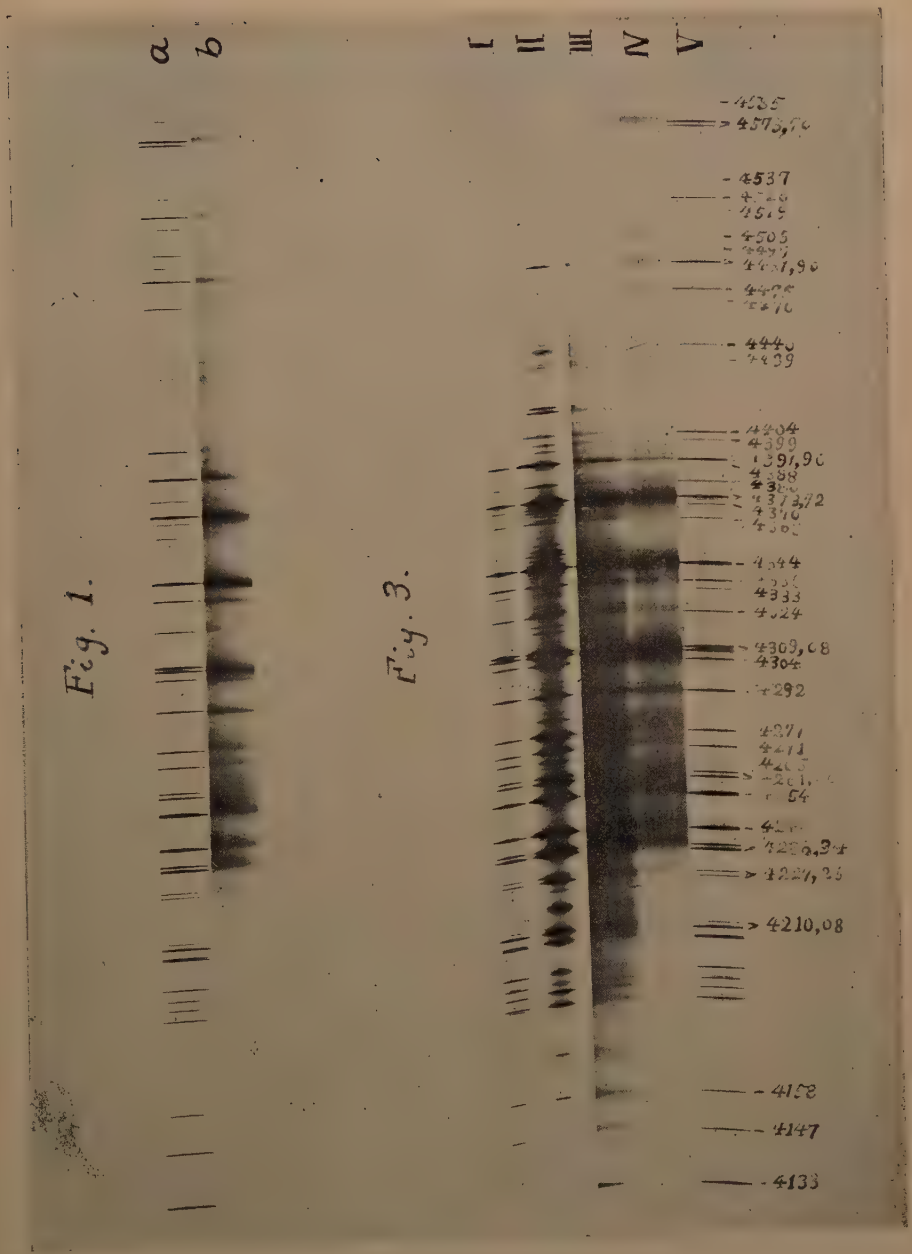
He considered that these large displacements of lines were caused solely by the changes in the temperature of the gas. But it seems to us that this phenomenon might be explained as the Stark broadening due to the field of ions in the large current flowing through the gas, as the current density in the case of the Geissler tube discharge was about 1·5 m. amp. per square mm., while in the spark discharge in chlorine gas at an atmospheric pressure, this was about 120 m. amp. per square mm.

Summary

1. Certain lines in the spectrum of chlorine were found to shift when the pressure of chlorine gas increased.

2. These lines were classified into three types, some of the lines belonging to one class suffering a shift of about 2 Å towards the red side.

The writer's sincere thanks are due to Professor M. Kimura for his kind guidance.


a
b
Fig. 1.
I
II
III
IV
V
Fig. 3.
4537
4505
4444
4399
4391,96
4333
4224
4309,08
4304
4292
4271
4211
4210,08
4158
4147
4133

Reversing Action of Red and Infra-red Rays on Sensitised and Fogged Photographic Plates and the Absorption of the Sensitising Dye-stuffs.

By

Michika Miyanishi.

(Received November 30, 1925)

ABSTRACT.

With a photographic plate sensitised with iodo-green and ogged by candle-light, Terenin has obtained reversed spectra of the red and the infra-red rays up to 1·13 μ. In the presnent experiment the relation between the absorption of the various sensitising dye-stuffs and the reversing action of the red and the infra-red rays was examined, and it was found that dye-stuff which has a strong absorption band in the region of wave-lengths longer than 5500 A. U. is effective in obtaining the reversed impression. As to the nature of the fogging light, green light seems to be most effective for plates sensitised with iodo-green.

It is known that when a photographic plate sensitised with malachite-green is fogged by candle-light, the photographic impression produced by the fogging is destroyed by exposing the plate to infra-red rays. This fact was applied by Millochau[1] to the photography of infra-red spectra, and he succeeded in photographing the solar spectrum from 7500 to 9500 A. U. Quite recently this problem was again investigated by Terenin.[2] His methode of preparing the plate is as follow: 50 c. c. of ethyl-alcohol was mixed with 100 c. c. of water. One gram of iodo-green was dissolved in 100 c. c. of water, and 6. c. c. of this solution was added to the former mixture. A very sensitive photographic plate was immersed in this solution for 5 minutes, and after drying it was fogged by candle-

1. C. R., **144**, 725 (1907).
2. Zeit. f. Phys., **23**, 5 (1924).

light. With the fogged plate thus prepared, he succeeded in photographing the reversed infra-red spectra up to 1·13 μ by using a prism spectrograph.

The present writer examined the relation between the spectral region reversed by red and infra-red rays and the position of the absorption bands of various dye-stuffs used for the sensitizer. As sensitizers, iodo-green, malachite-green, methyl-green, ethyl-violet, nigrosin, fuchsin f. Bac., auramin, cyanin, and erythrosin were used. Pieces of Ellington Studio plate were sensitized with these dye-stuffs and then fogged by candle-light after being dried, following the prescription given by Terenin. The fogged plate thus prepared was placed in a plate holder of a prism spectrograph provided with a photographic lens of 50 cm. focus, and the light emitted from a carbon arc charged with salts of potassium and barium was focussed on the slit of the spectro-graph through a ruby glass filter. It was found that the spectrum was reversed in the region from λ 7500 to 9000 on the plate treated with iodo-green, malachite-green, methyl-green, ethyl-violet, auramin, nigrosin, and fuchsin respectively, and in the region about λ 8500 on the plate treated with auramin. No reversal was, however, found on the plates treated with the remaining dyes: they give only positive impressions of lines up to λ 7500 or 8500. These will be seen from the photographs given in Fig. 1, reversed lines appearing as black lines.

The difference shown by plates sensitised with the above dyes is probably due to the difference in the absorption bands possessed by these dyes. Such bands are shown diagrammatically in the curves given in Fig. 2, curves drawn above the horizontal lines respectively being roughly the absorption bands, and those below, the reversed spectral regions in the plates treated by such dyes.

It will be observed that dye-stuffs having an absorption maximum in the neighbourhood of λ 5500 to 6000 are effective in reversing the spectral lines in the infra-red region. Such was the case for iodo-green, malachite-green, methyl-green, ethyl-violet, nigrosin and fuchsin. Cyanin and erythrosin have an absorption maximum in the neighbourhood of λ 5000, but they have no such reversing property. Auramin shows a very interesting example. This has weaker absorption in the region from λ 6000 to 5500 and stronger one in the region from λ 5000 to 4700. The plate treated with this dye showed a weaker reversal in the neighbourhood of λ 8500 and this reversal was probably due to the weak absorption possessed by the dye in the region from λ 5500 to 6000.

The photographic plates sensitized with iodo-green were fogged separa-

tely by the light from an incandescent electric lamp filtered through a Wratten monochromatic filter, the time of exposure and intensity of coloured lights being so adjusted that each plate had stronger, medium and weaker foggings, and their corresponding densities were nearly equal for all the plates. The accompanying table shows the data for the exposure.

Transmission of the filter	Distance between the lamp and the plate	Time of the fogging exposure		
		Stronger	Medium	Weaker
Red	12 cm.	5 minutes	4 minutes	3 minutes
Orange	14 〃	4 〃	3 〃	2 〃
Yellowish green	16 〃	4 〃	3 〃	2 〃
Green	18 〃	4 〃	3 〃	2 〃
Blue	19 〃	4 〃	3 〃	2 〃
Violet	20 〃	3 〃	2 〃	1 〃

The plates thus treated were exposed to light from the electric arc through the spectroscope, and the intensities of the reversed spectral lines were raughly compared. The experiment is of rather a preliminary nature, but the result seems to indicate that the plate fogged strongly by the light filtered through the green screen gives the best result, recording the lines up to λ 9500. Photographs reproduced in Fig. 3 illustrate this.

Lastly, it will be interesting to mention, that when a plate sensitised with iodo-green was fogged by violet light, an isolated reversed impression of spectral lines was noted about 6400 A. U. in addition to the ordinary reversed spectra.

In conclusion, the writer wishes to express his best thanks to Prof. M. Kimura, under whose guidance the present experiments were carried out.

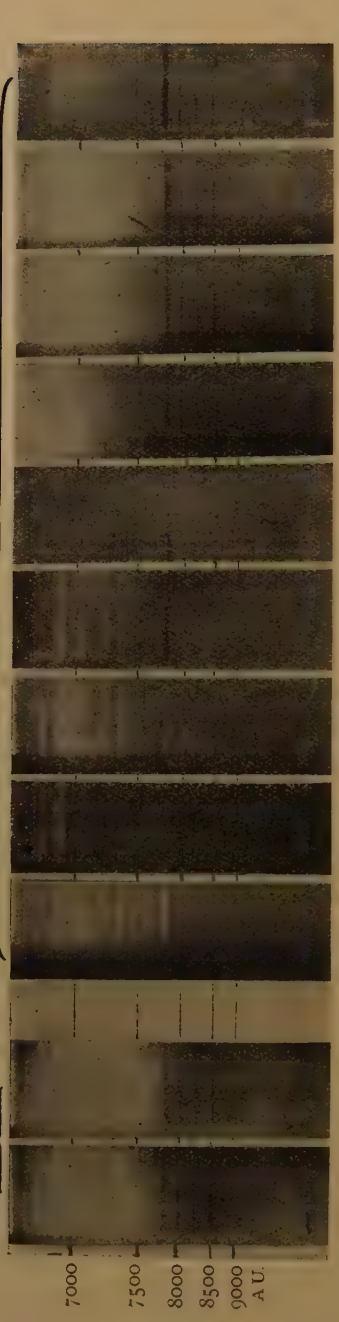
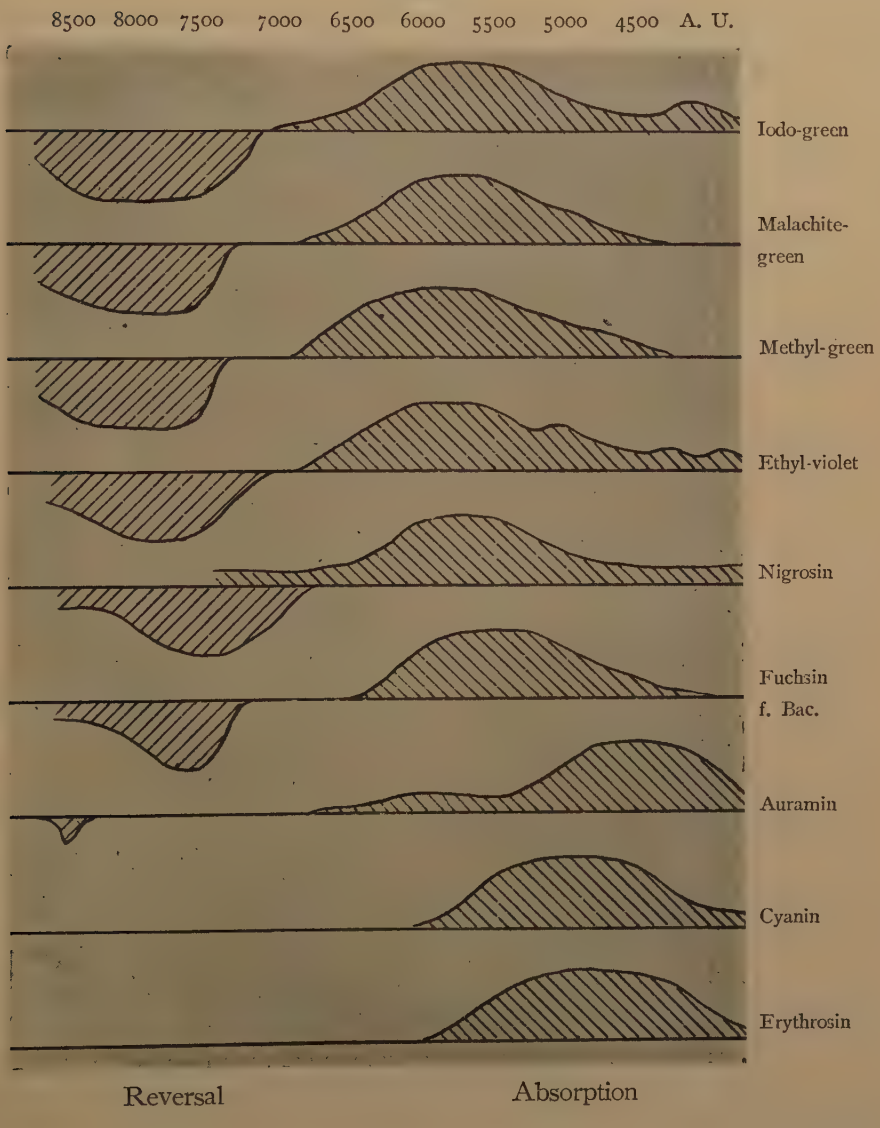

Dye-stuff used
Iodo-green
Malachite-green
Methyl-green
Ethyl-violet
Nigrosin
Fuchsin f. Bac.
Auramin
Cyanin
Erythrosin
Sensitized by iedo-green and fogged by light of yellowish green colour,
green colour
7000
7500
8000
8500
9000
A.U.

Fig. 1.

Fig. 3.

Fig. 2.


8500 8000 7500 7000 6500 6000 5500 5000 4500 A. U.
Iodo-green
Malachite-green
Methyl-green
Ethyl-violet
Nigrosin
Fuchsin f. Bac.
Auramin
Cyanin
Erythrosin
Reversal
Absorption

Self-reversal of Lines in the Explosion Spectrum of Tin.

By

Bunsaku Arakatsu and Masaru Shoda.

(Received November 30, 1925)

The explosion spectra of lead and tin, as elements belonging to the fourth group of the periodic table, were studied. The mode of the appearance of the reversed lines in the spectrum of the former element has already been described by one of us in a previous paper.[1]

The explosion spectrum of tin was studied in the same way as described in the experiment with lead. Almost all of the arc lines of tin whose wave-lengths are shorter than 3200 A were self-reversed. The order of the appearance of such lines was determined by varying the pressure of the air surrounding the exploded tin wire.

The spectrogram shows that all the lines were sharp when the explosion took place in vacuo, but on increasing gradually the pressure of the surrounding air certain lines became first broader and then self-reversed. The lines were therefore classified into four groups, as shown in the table, according to the stages in which the reversal appeared.

As the series relation of the arc lines of this element together with the other members of the fourth group are not yet completely established, it is not superfluous to compare our results with the series relations recently proposed by J. C. McLennan.[2]

The lines reversed in the first stage are λ 2429·6* ($2p_1 - 3d_1$), λ 2354·9

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1 These Memoirs, **9**, 451 (1926).

2 Trans. R. Soc. Canada. **3** (1924).

$(2p_2-3d_3)$, λ 2317·3* (x_2-4d_1), λ 2269·0*,
λ 2246·2 $(2p_3-3d_2)$, and λ 2096·3;
the lines marked with * are not given in McLennan's list of the absorption spectrum of the normal vapour in a quartz cell.[1]

Thus, certain lines belonging to the diffuse series together with some non-series lines appeared as reversals in the first stage. The relation among the spectral terms p_1, p_2, p_3, and x_1, x_2, x_3, with respect to the order of the appearance of the reversal is not so obvious as in the case of lead, but the interesting fact is that the above mentioned series lines have the smallest wave-length in the lines belonging to the same diffuse term, e.g. λ 2354·8 $(2p_2-3d_3)$ is the most refrangible one in the lines x_n-3d_3 and $2p_n-3d_3$, and also λ 2429·5 $(2p_1-3d_1)$ is the most refrangible in the lines having the $3d_1$ term.

This lines reversed in the second stage are
λ 3034·2, λ 2863·4 $(2p_3-2_s)$, λ 2840·1, λ 2706·6 and λ 2421·8*.

The third and the fourth stage reversals were not so distinctly defined as the first and the second stage reversals.

Of the lines belonging to x_n-2s and $2p_n-2s$, the reversal appeared first in the line λ 2863·4 $(2p_3-2s)$ and then proceeded to the lines $2p_1-2s$ and $2p_2-2s$.

The lines belonging to $2p_n-3s$ reversed at a later stage than the lines $2p_n-2s$. This fact is quite in harmony with the result obtained by M. Kimura.

As in the case of lead, the width of lines belonging to $2p_n-ms$ is not symmetric with respect to the absorbed part, the red side of the absorption being more broadened.

The spark line λ 2209·6 is found to be reversed in the third stage.

The results are smmarised in the Table and the Plate. Thus we see that, in general, the relation between the spectral terms p_1, p_2, p_3 with respect to the order of the appearance of the reversal is not so regular as in the case of lead.[2]

Finally it is to be noticed that, besides the lines appearing in the absorption spectrum of the heated normal vapour, many lines which show no reversal in it reversed strongly in our explosion spectrum. This forces us to think that the reversal appearing in our explosion spectrum is originated not only by the mere absorption of the heated vapour, but by the absorp-

1 loc. cit.
2 loc. cit.

tion of the excited atoms in the strong electric field.[1]

The authors wish to express their thanks to Prof. M. Kimura who encouraged them by his valuable advice throughout this experiment.

The authors' thanks are also due to President T. Maruyama of the Konan College, through whose good offices the experiment was carried out.

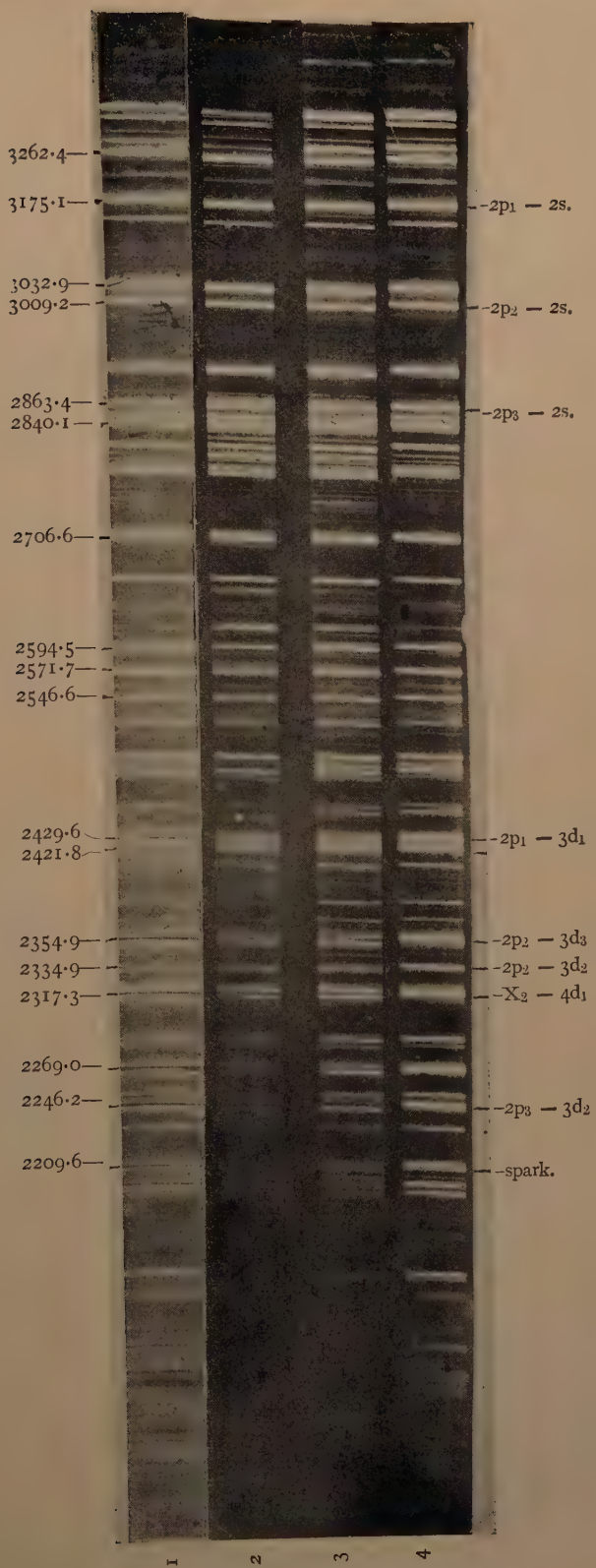
Table.

Absorption of normal Vapour in a Quartz Cell (McLennan) (I. A.)	Reversal in a heavy Arc (McLennan) (I. A.)		Reversal in an Explosion Spectrum (A and S)		Series
				Order of Reversal	
——			3262·4	3	——
3175·04			3175·1	2	$2p_1 - 2s$
3034·12			3034·2		——
——			3032·9	2	——
3009·14			3009·2	3*	$2p_2 - 2s$
2863·32			2863·4	2	$2p_3 - 2s$
——			2850·7	4	——
2839·98			2840·1	2	——
2706·50			2706·6	2	——
——			2594·5	4	$X_1 - 6d_3$
			2571·7	3	——
2546·55			2546·6	3	
——			2495·8	4	——
2483·39			2483·5	4	——
——			2429·6	1	$2p_1 - 3d_1$
			2421·8	1	——
——			2354·9	1	$2p_2 - 3d_3$
2354·84			2334·9	2	$2p_2 - 3d_2$
2334·80			2317·3	1	$X_2 - 4d_1$
——			2286·8	3	——
			2282·4	4	——
			2269·0	1	——
	——	——	2267·3	3	——
——	2251·12	4R	2251·3	4	$X_2 - 4s$
2246·02	2245·95	10R	2246·2	1	$2p_3 - 3d_2$
2231·68	2231·73	4R	2231·8	4	$2p_1 - 3s$
2220·84?					
2209·60	2209·62	6R	2209·6	3	Spark

1 loc. cit.

Absorption of normal Vapour in a Quartz Cell (McLennan) (I. A.)	Reversals in a heavy Arc (McLennan) (I. A.)		Reversals in an Explosion Spectrum (A and S)		Series
				Order of reversal	
2199·29	2199·29	8R	2199·3	3	(Spark)
2194·42	2194·46	6R	2194·5	3	(Spark)
2171·43	2171·24	2R	2171·2	3	(Spark)
	2151·31	5R	2151·3	4	——
	2148·64	5R	2148·6	3	$2p_2 - 3s$
	2121·15	2R	2121·2	4	$X_2 - 6d_2$
	2113·85	4R	2113·9	?	$X_3 - 4d_3$
	2100·84	4R	2100·9	?	$2p_1 - 4d_3$
	2096·30	4R	2096·3	?	$X_2 - 6s$
	2094·25	3R	2094·3	?	$2p_1 - 4d_2$
	2091·61	2R	2091·6	?	——
	2080·57	3R	2080·6	?	$X_2 - 7d_3$
	2072·92	4R	2072·9	?	$2p_3 - 3s$
	2068·55	4R	2068·6	?	$2p_1 - 4d_1$
	2064·01	3R	.....		
	2058·24	3R	.....		
	2053·47	3R	.....		

Explosion Spectrum of Tin.



1. Explosion in the air
2. " Pressure 76 cm. of Hg.
3. " 60 cm. "
4. " 50 cm. "
" 40 cm. "

On the System of Orbital-planes in the Inner Region of an Atom, and on the O-Triplets in X-Ray Spectra belonging to the L-Series.[1]

By

Hideki Hirata.

(Received November 11, 1925)

Abstract

Sommerfeld's theory of the elliptic orbits is modified, by making use of three quantum numbers corresponding to three co-ordinates in space. From the standpoint of this theory a selection principle of the transition of electrons in the inner region of an atom is proposed on the one hand; and on the other hand a discussion is made on the formation of O-triplets in X-ray spectra.

To begin the discussion, let us start from the assumption that the following postulates hold good at least in the inner region of an atom, which is responsible for X-ray radiations.

I. The stationary orbit of every electron in an atom is a plane orbit, and the stationary orbits taken by the majority of the electrons in an atom are situated in the same plane.

II. Sommerfeld's quantizing principle [Quantenansatz] and its consequential theory of the elliptic orbits govern the motion of each electron separately.

In the following articles, some slight modifications of Sommerfeld's theory are described, which is founded on the above two postulates, and their consequences are compared with the experimental results.

§ 1. *The Energy of Kepler's Motion of an Electron in the Atom.*

1 This was read before the Physico-Mathematical Society of Japan, April, 1923, and a brief account of that address is published in the Proceedings of that Society, 3rd Ser., Vol. 5, No. 4, 1923. A slight modification is made in the present paper with regard to the "quintets" noted at that time.

The qualitative and quantitative arguments in connection with Kepler's motion of an electron in an atom of the so-called "Wasserstoffähnlich" elements were put forward by Sommerfeld[1]. Now, mainly following him, let us start to get, in reference to any element, the general expression of the energy of Kepler's motion of an electron revolving in the inner region of an atom.

Let f be the degree of freedom of the system under consideration q_i the configurational co-ordinate, T the kinetic energy expressed as a function of q_i and $\dot{q}_i$, and $p_i = \frac{\delta T}{\delta \dot{q}_i}$ the corresponding impulse co-ordinate. Then, Sommerfeld's quantizing principle, for each one of the f pairs of co-ordinates (p_i, q_i), can be expressed

$$(1) \qquad \int p_i \, dq_i = nh \qquad i = 1, 2, 3, \ldots\ldots\ldots\ldots f.$$

where h: Plack's constant $= 6{\cdot}55 \times 10^{-27}$ erg. sec.

n: positive integer, independently chosen for each degree of freedom.

As to the integration limits to be adopted in formula (1), Sommerfeld states that "Every co-ordinate q_i must be taken over the whole region [Bereich] which belongs to the unique representation of the phases of the system."

In the present case, the mass of the electron or the planet is regarded as infinitely small in comparison with that of the nucleus or the sun, so that there is no necessity to take the motion of the nucleus into account. Moreover, as the magnitude of the electron is very small compared with that of the atom, it is treated as a material point.

In an atom which has only one electron in it, as in the cases of hydrogen, ionized helium, etc., the state of the electron is determined by two conditions; e.g., the distance from the centre of the nucleus to the electron and the azimuth angle of the electron on the stationary orbit measured from the abhelion or the perihelion of the orbit. On the other hand, in the case of an element of large atomic weight which has many electrons in its atom, the above consideration can no more be held. To determine the state of each electron in its stationary orbit, besides the two co-ordinate above stated, one more co-ordinate is needed, to determine the inclination of the orbital plane. In short, the state of the electron has three degrees of freedom in such a case. Thus, it is necessary in such a case to select one special plane as the equatorial plane from which the inclination of the orbital plane or the ecliptic plane is measured. Fortunately, according to the foregoing postulate I, we can select the plane in which the

1 Ann. d. Phys. **51**, 44, (1916).
Atombau u. Spektrallinien, 3 Aufl., Kap. 8.

orbits taken by the majority of the electrons are situated.

Fig. 1 is taken from Sommerfeld's paper. Adopting the atomic model of the coplaner orbits of the electrons, he used this figure for the purpose of explaning the Zeeman effect.

In this Fig. 1, ON and OM are the normals to the equatorial plane OKQ and to the ecliptic plane OKP respectively; both of them pass through the centre of the nucleus O. The straight line OK is the intersection of the equatorial and the ecliptic plane, and α_1 is the angle between them. Let P be the instantaneous position of the electron, the intersection of the ecliptic plane with the unit sphere is expressed by a great circle KPAB.

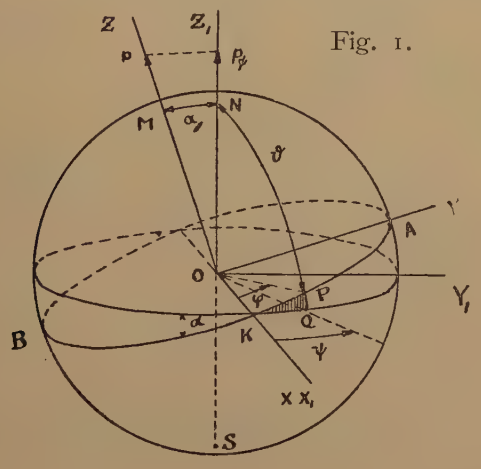


Fig. 1.

To represent the position P of the electron under consideration, let us adopt a spatial polar co-ordinate system ($\Psi.\vartheta.$ r) and a rectangular co-ordinate system (x. y. z.) having the origin O in common. The axis of the former is taken as to be in coincidence with ON, while X and Z, axes of the latter, coincide with OK and OM respectively. Then we have, as the consequence of (1), the three quantizing equations corresponding to the three co-ordinates.

i. e.,
$$\left.\begin{aligned} \int p_r dr &= n'h \\ \int p_\psi d\psi &= n_1 h \\ \int p_\vartheta d\vartheta &= n_2 h \end{aligned}\right\} \quad (2)$$

where
$$\left.\begin{aligned} p_r &= \frac{\delta T}{\delta \dot{r}} = m\dot{r} \\ p_\psi &= \frac{\delta T}{\delta \dot{\psi}} = mr^2\dot{\psi}\sin^2\vartheta \\ p_\vartheta &= \frac{\delta T}{\delta \dot{\vartheta}} = mr^2\dot{\vartheta} \end{aligned}\right\} \quad (3)$$

According to our postulate I, we can put

$$p = \frac{\delta T}{\delta \dot{\varphi}}$$

where φ: azimuth angle of the electron on the ecliptic plane.

From these equations, the following expression can easily be obtained by simple calculations concerning the spherical triangle KPQ

$$\left.\begin{aligned} \int p_\vartheta d\vartheta &= 2\pi p\,(1 - \cos a_1) = n_2 h \\ \int p_\psi d\psi &= 2\pi p \cos a_1 = n_1 h \end{aligned}\right\} \quad (4)$$

Thus, $$\int p_\vartheta d\vartheta + \int p_\psi d\psi = (n_1 + n_2)\, h = 2\pi p \quad (5)$$

As the point P is always situated on the x-y plane, z and z should always be z=o, and $\dot{z}$ =o. Consequently, the equations of motion of the electron should take the same forms as those of Sommerfeld's.

At first, disregarding the effect due to the repulsion of the fellow electrons, let us take only the electrostatic attraction between the nucleus and the electron into account.

Then the toral amount of the energy W possessed by the electron should be the same as that of the mono-electronic elements calculated by Sommerfeld.

i. e., $$W = m_0 c^2 \left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) - \frac{eE}{r} \quad (6)$$

where m_0 is constant and equal to the mass of the electron at rest,

$$\beta = \frac{v}{c}$$

v is the instantaneous velocity of the electron,

c is the velocity of light = 3×10^{10} cm. sec^{-1}.,

e is the electronic charge,

E is the charge of the nucleus.

From the solution of the equations of motion given by Sommerfeld, the expression (6) can be transformed into the form.

$$1 + \frac{W}{m_0 c^2} = \left(1 + \frac{(1-\varepsilon^2)\, p_0^2}{p^2 - p_0^2}\right)^{-\frac{1}{2}} = \left(\frac{p^2 - p_0^2}{p^2 - \varepsilon^2 p_0^2}\right)^{\frac{1}{2}} \quad (7)$$

where $$p_0 = \frac{eE}{c}$$

ε is the eccentricity of the orbit.

Further, the quantizing condition concerning to the eccentricity of the orbit gives[1]

1 A. Sommerfeld: Ann. d. Phys., **51**, 53 (1916).

$$2\pi p\gamma\left(\frac{1}{\sqrt{1-\varepsilon^2}}-1\right)=2\pi\sqrt{p^2-p_0^2}\left(\frac{1}{\sqrt{1-\varepsilon^2}}-1\right)=n'h \quad (8)$$

where $$\gamma^2=1-\left(\frac{eE}{pc}\right)^2 \quad (9)$$

From (5) and from the above expression (8) we get, by putting $$a=\frac{2\pi e^2}{hc}, \quad (10)$$

$$\sqrt{p^2-p_0^2}=\frac{n_1+n_2}{2\pi}h\sqrt{1-\frac{p_0^2}{p^2}}=\frac{n_1+n_2}{2\pi}h\sqrt{1-\left(\frac{a}{n_1+n_2}\frac{E}{e}\right)^2},$$

$$\frac{1-\varepsilon^2}{p^2-p_0^2}=\frac{1}{\left(\frac{n'h}{2\pi}+\sqrt{p^2-p_0^2}\right)^2}$$

$$=\frac{\left(\frac{2\pi}{h}\right)^2}{\left[n'+(n_1+n_2)\sqrt{1-\left(\frac{a}{n_1+n_2}\frac{E}{e}\right)^2}\right]^2}, \quad (11)$$

Substituting the above values of (11) into (7), we get

$$1+\frac{W}{m_0c^2}=\left\{1+\frac{\left(a\frac{E}{e}\right)^2}{\left[n'+(n_1+n_2)\sqrt{1-\left(\frac{a}{n_1+n_2}\frac{E}{e}\right)^2}\right]^2}\right\}^{-\frac{1}{2}}$$

$$=1-\frac{1}{2}\frac{a^2}{A^2}\left(\frac{E}{e}\right)^2+\frac{3}{8}\frac{a^4}{A^4}\left(\frac{E}{e}\right)^4-\frac{5}{16}\frac{a^6}{A^6}\left(\frac{E}{e}\right)^6$$

$$+\frac{35}{128}\frac{a^8}{A^8}\left(\frac{E}{e}\right)^8-\cdots\cdots\cdots\cdots\cdots \quad (12)$$

where $$A=n'+(n_1+n_2)\sqrt{1-\left(\frac{a}{n_1+n_2}\frac{E}{e}\right)^2}$$

Let N be Rydberg's frequency

$$N=\frac{2\pi^2m_0e^4}{h^3}=1097\ 37\text{cm.}^{-1}$$

Then, the total energy of the electron should be

$$W=-Nh\left(\frac{E}{e}\right)^2\left\{\frac{1}{A^2}-\frac{3}{4}\frac{a^2}{A^4}\left(\frac{E}{e}\right)^2+\frac{5}{8}\frac{a^4}{A^6}\left(\frac{E}{e}\right)^4\right.$$

$$\left.-\frac{35}{64}\frac{a^6}{A^8}\left(\frac{E}{e}\right)^6+\cdots\cdots\right\} \quad (13)$$

By expanding every term of the right side of the above expression (13)

in an ascending power-series of α^2 and adding together, we get the following energy expression

$$W = -\frac{Nh}{(n_1+n_2+n')^2}\left(\frac{E}{e}\right)^2\left[1+\frac{1}{4}\frac{\alpha^2}{(n_1+n_2+n')^2}\left(\frac{E}{e}\right)^2\left\{1+4\frac{n'}{n_1+n_2}\right\}+\frac{1}{8}\frac{\alpha^4}{(n_1+n_2+n')^4}\left(\frac{E}{e}\right)^4\left\{1+6\frac{n'}{n_1+n_2}+12\left(\frac{n'}{n_1+n_2}\right)^2+2\left(\frac{n'}{n_1+n_2}\right)^3\right\}+\frac{1}{64}\frac{\alpha^6}{(n_1+n_2+n')^6}\left(\frac{E}{e}\right)^6\left\{5+40\frac{n'}{n_1+n_2}+128\left(\frac{n'}{n_1+n_2}\right)^2+184\left(\frac{n'}{n_1+n_2}\right)^3+64\left(\frac{n'}{n_1+n_2}\right)^4+8\left(\frac{n'}{n_1+n_2}\right)^5\right\}+\cdots\cdots\cdots\cdots\right] \quad (14)$$

In the above expression (14), the total energy W can simply be expressed in the terms of $n_1+n_2=n$ and n'; it is not necessary to express it by using the three quantum numbers n_1, n_2, and n' separately. Thus, at first sight, it seems quite meaningless to consider such an orientation of the orbital plane in space. But in reality, the above expression (14) has its foundation on the assumption that there is no effect due to the repulsion of the fellow electrons on the revolving electron and consequently E is a constant for any orbit in the atom.

If we take into account such effects, some corrections should be needed. It will appear later that E in (14) should express the so-called "effective nuclear charge" and should be a function of n_1 n_2, and n' except in the case of the mono-electronic elements.

Now if we express the effective nuclear charge of the electronic orbit of quantum numbers n_1, n_2, n' by $E(n_1, n_2, n')$, then the energy expression $W(n_1, n_2, n')$ corresponding to the "Term" of Sommerfeld's fine structure theory becomes.

$$W(n_1, n_2, n') = -\frac{Nh}{(n_1+n_2+n')^2}\left(\frac{E(n_1\ n_2,\ n')}{e}\right)^2\left[1+\frac{1}{4}\frac{\alpha^2}{(n_1+n_2+n')^2}\left(\frac{E(n_1,\ n_2,\ n')}{e}\right)^2\left\{1+4\frac{n'}{n_1+n_2}\right\}+\frac{1}{8}\frac{\alpha^4}{(n_1+n_2+n')^4}\left(\frac{E(n_1,\ n_2,\ n')}{e}\right)^4\left\{1+6\frac{n'}{n_1+n_2}+12\left(\frac{n'}{n_1+n_2}\right)^2+2\left(\frac{n'}{n_1+n_2}\right)^3\right\}+\cdots\cdots\cdots\cdots\right] \quad (14b)$$

Atomic Number	ι (ε)	α_2 (α')	α_1(α)	α_3(α'')	η (η)	β_4(φ')	β_6 (ι)	β_1(β)	β_5(ϖ)	β_2(γ)
29 Cu	—	—	68·47	—	—	—	—	—	—	—
30 Zn	—	—	74·55	—	—	—	—	76·25	—	—
32 Ge	—	—	87·50	—	—	—	—	—	—	—
33 As	—	—	94·42	—	—	—	—	97·00	—	—
34 Se	—	—	101·58	—	—	—	—	104·53	—	—
35 Br	—	—	109·04	[109·41]$_s$	—	—	—	112·39	—	—
37 Rb	—	—	124·78	[125·28]$_s$	—	—	—	129·06	—	—
38 Sr	—	—	133·07	—	—	—	—	137·87	—	—
39 Y	—	—	141·61	[142·12]$_s$	—	—	—	147·01	—	—
40 Zr	—	—	150·47	[151·08]$_s$	—	—	—	156·50	—	—
41 Nb	—	159·4	159·55	[159·96]$_s$	—	—	—	166·29	—	172·09
42 Mo	—	168·7	168·93	[169·54]$_s$	—	—	—	176·40	—	—
44 Ru	—	188·13	188·44	[189·28]$_s$	—	—	—	197·62	—	—
45 Rh	—	198·29	198·62	[199·43]$_s$	—	—	—	208·77	—	—
46 Pd	—	208·69	209·07	[209·70]$_s$	—	224·1	—	220·25	226·4	233·7
47 Ag	—	219·37	219·80	[220·50]$_s$	—	236·01	—	232·06	238·27	246·69
48 Cd	—	230·32	230·82	—	—	248·00	—	244·29	250·59	259·8
49 In	—	241·55	242·12	—	—	—	—	256·84	—	273·5
50 Sn	—	253·06	253·69	—	—	273·4	—	269·79	276·35	287·59
51 Sb	—	264·84	265·53	—	—	286·5	—	283·13	289·73	302·0
52 Te	—	276·91	277·67	—	—	299·77	—	296·85	303·65	316·7
53 J	—	289·23	290·07	—	—	313·6	—	310·94	317·8	331·87
55 Cs	—	314·73	315·76	—	—	342·55	—	340·33	347·46	363·5
56 Ba	—	327·94	329·05	—	—	357·38	—	355·64	362·89	379·80
57 La	—	341·47	342·66	—	—	372·86	—	371·48	378·90	396·5
58 Ce	—	355·28	356·57	—	—	388·57	—	387·66	395·40	413·6
59 Pr	—	369·33	370·82	—	—	404·3	—	404·36	412·14	431·00
60 Nd	—	383·64	385·31	—	—	421·5	—	421·50	429·44	448·8
62 Sm	—	413·22	415·21	—	—	—	—	457·17	465·4	485·5
63 Eu	—	428·42	430·65	—	—	474·4	—	475·61	483·2	504·3
64 Gd	—	444·02	446·34	—	—	493·0	—	494·68	503·8	523·3
65 Tb	—	459·78	462·30	—	471·4	511·6	—	514·16	523·05	542·78
66 Dy	—	475·79	478·54	—	—	530·5	—	534·09	542·6	562·71
67 Ho	—	492·12	495·09	—	—	551·3	—	554·58	563·75	582·91
68 Er	—	508·78	511·93	—	529·2	571·1	—	575·63	585·5	603·16
70 Ad	482·2	542·90	546·51	—	563·9	612·5	—	619·0	629·1	645·4
71 Cp	498·0	560·43	564·20	—	—	635·6	—	642·9	653·4	667·2
73 Ta	528·50	595·83	600·20	—	621·83	678·93	686·87	688·51	699·23	711·42
74 W	544·02	613·85	618·45	—	642·78	701·66	708·03	712·39	723·23	733·76
76 Os	—	651·75	656·45	—	—	748·25	756·33	762·83	774·08	780·58
77 Ir	—	670·35	675·84	—	—	774·62	777·75	788·99	800·82	804·39
78 Pt	608·64	689·73	695·58	—	734·82	799·52*	799·52*	815·65	828·80*	828·80*
79 Au	625·63	709·22	715·53	—	759·97	825·15	820·51	843·02	—	853·46
80 Hg	—	—	—	—	—	—	—	[868·7]$_s$	—	[872·66]$_s$
81 Tl	—	749·39	756·42	—	810·30	878·64	869·49	899·88	913·23	904·16
82 Pb	676·70	769·96	777·51	—	835·90	907·01	894·50	929·98*	943·30	929·98*
83 Bi	694·07	790·20	798·54	—	862·32	934·22	918·97	959·93	973·85	956·28
84 Po	—	—	[832·5]$_s$	—	—	—	—	[990·5]$_s$	—	—
88 Ra	—	—	[906·5]$_s$	—	—	—	—	—	—	—
90 Th	819·19	944·08	955·78	—	—	1155·00	1102·78	1194·94*	1211·67	1151·93
92 U	855·84	990·37	1003·23	—	1134·95	1222·53	1158·70	1269·08	1286·29	1210·70

$\frac{\nu}{N}$ in the L Series.

β_7	β_5 (ζ)	β_9	β_3 (o,s)	γ_5 ($\varkappa$)	γ_1 (δ)	γ_7	γ_6 (ϑ)	γ_2 (χ')	γ_3 (χ)	γ_4 (Ψ)
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
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—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	193·42	—	—	—	—	—
—	—	—	—	—	218·38	—	—	—	—	—
—	—	—	—	—	231·53	—	—	—	—	—
—	—	—	—	—	245·19	—	—	253·6*	253·6*	—
—	—	—	—	—	259·15	—	—	—	—	—
—	—	—	—	—	273·81	—	—	—	—	—
—	—	—	—	—	288·79	—	—	—	—	—
—	—	—	—	—	304·29	—	—	314·6	315·8	322·3
—	—	—	—	—	320·29	—	—	328·0*	328·0*	—
—	—	—	—	—	336·73	—	—	—	—	—
—	—	—	—	—	353·59	—	—	—	—	—
—	—	—	—	—	389·05	—	—	406·1*	406·1*	—
—	—	—	—	—	407·48	—	—	—	—	—
—	—	—	—	—	426·45	—	—	—	—	—
—	—	—	—	—	445·8	—	—	456·8*	456·8*	—
—	—	—	—	—	465·77	—	—	471·80	473·29	—
—	—	—	—	—	486·40	—	—	506·2*	506·2*	514·0
—	—	—	—	—	528·96	—	—	550·1*	550·1*	—
—	—	—	—	—	549·2	—	—	570·1	573·8	—
—	—	—	—	—	573·75	—	—	586·5	588·3	—
—	550·2	—	—	—	596·1	—	—	618·2	620·9	635·2
—	—	—	—	—	621·2	—	—	642·2	644·0	—
—	—	—	—	—	645·4	—	—	667·3	669·3	—
—	—	—	—	—	668·4	—	—	690·5	694·0	—
—	—	—	—	—	720·4	—	—	743·6	746·2	—
—	—	—	—	—	746·9	—	—	769·6	772·5	—
23·30	728·65	—	—	778·86	803·04	—	820·98	826·90	831·28	857·74
46·45	751·56	(753·74)o	(785·87)s	807·03	831·81	(845·18)o	854·08	854·98	859·97	887·77
—	—	—	—	—	891·25	—	—	—	—	—
—	—	—	—	—	921·96	—	945·64*	945·64*	952·64	—
44·93	851·57	—	[850·1]s	924·71	953·77	—	978·07*	978·07*	984·52	1018·17
70·77	877·70	—	[880·5]s	955·01	985·83	—	1011·12*	1011·12*	1017·41	1051·86
—	—	—	—	—	1011·46	—	—	—	—	—
22·64	931·47	—	[932·7]s	1019·14	1053·12	—	1082·69	1078·83	1087·54	1125·00
50·22	959·72	—	—	1054·83	1088·37	—	1119·97*	1113·87	1119·97*	1162·89
—	987·98	—	[987·3]s	1087·75	1124·10	—	1157·55*	1149·20	1157·55*	1196·89
—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—
—	1194·94*	—	—	—	1399·74	—	1146·20	—	—	—
38·14	1258·43	—	—	—	1486·98	—	1537·76	1507·82	1526·41	—

§ 2. *The Lines belonging to the L Series and their Wavelengths*

The X-ray spectra, as are well known, consist of three groups of lines. i. e., the K, L, and M Series.

If we mention the lines in order of their wavelengths (Roughly because some lines interchange their positions owing to the different elements), we get for

the K Series: $K\alpha_2$, $K\alpha_1$, $K\beta_3$, $K\beta_1$, $K\beta_2$;

the L Series: Ll, $L\alpha_2$, $L\alpha_1$, $L\alpha_3$, $L\eta$, $L\beta_4$, $L\beta_6$, $L\beta_1$ $L\beta_3$, $L\beta_2$, $L\beta_8$ $L\beta_7$, $L\beta_5$, $L\beta_9$, $L\beta_{5(o,s)}$ $L\gamma_5$, $L\gamma_1$, $L\gamma_7$, $L\gamma_6$, $L\gamma_2$, $L\gamma_3$, $L\gamma_4$;

the M Series: $M\alpha_2$, $M\alpha_1$, $M\beta$, $M\gamma$, $M\delta$, $M\varepsilon$.

With regard to the wavelengths of the L series many experimental data have been obtained by numerous investigators. Among these data let us select the up-to-date values given in A. Sommerfeld's paper[1] concerning the elements lighter than tantalium, while concerning the heavier elements let us select the values given in D. Coster's paper[2], as the latter seems to me quite complete for all the elements between tantalium and uranium; and let us rely on them in our further arguments.

From these numerical values of the wavelengths, we can get the values of $\frac{\nu}{N}$ as shown in Table I, where ν is the wave number in cm^{-1} and N the Rydberg's constant, which is equal to 109737 cm^{-1}.

In this table, the values in ( )$_0$, ( )s, are interpolated from the measurements of Overn[3] and Siegbahn[4], and those in [ ]s are taken from the old data of Siegbahn and Friman[5].

To get rid of the effect of the general shift of all the experimental values of the wavelengths of the lines, due to the difference of the numerical values given to the grating constants of the crystals used, all these interpolations (except the spectra of P_o and R_a) & exterpolations are so made that the ratio of the distances between an interpolated line and its neighbouring lines on both sides is equal to the corresponding ratio in the data used, i. e., equal to the ratio of the distances between the original line to be interpolated and its neighbouring lines on both sides. To interpolate the lines $L\alpha_1$, and $L\beta_1$, of P_o and $R\alpha$, which have no neighbouring lines, we determine their wavelengths in such way that: with regard to every line to be interpolated (e. g. $L\alpha_1$), the ratio of the differences

1 Atombau u. Spektrallinien, 3 Aufl., 3 Kap., s. 200.
2 Z. S. f. Phys., **6**, 188, (1921).
3 Phys. Rev., **16**, 137, (1919).
4 Phil. Mag., **38**, 639, (1919).
5 Phys. Z. S., **17**, 17, 61, 176, (1916).
Ann. d. Phys., **49**, 623, (1916).

between the wavelength of that line ($L\alpha_1$) of the element P_o or $R\alpha$, and those of the same line ($L\alpha_1$) of the elements on both sides i, e., Bi and Th, remain the same as that of the original data (Siegbahn and Friman's data.).

The notations in ( ) on the right side of the names of lines are their other names given by Sommerfeld[1]. Among those lines, there is a line $L\beta_{5(o,s)}$ which is the line denominated $L\beta_5$ by Overn and Siegbahn.

§ 3. *On the Regular Doublets of X-Ray Spectra.*

The further arguments we now attempt to make, aim at the explanation of some experimental fact, by the adoption of our foregoing theory. Before entering into these arguments, however, it will be better to give the explanations of the so-called " regular doublets " in the X-ray spectra which have been excellently discussed by Sommerfeld in this theory of elliptic orbits.

Generally, let us consider the case when an electron falls down from the same initial stationary orbit to two adjacent final stationary orbits of the quantum numbers n_1, n_2, n', and m_1, m_2, m', respectively suddenly radiating out the differences of energy in the form of monochromatic radiations. In such a case, we can express, by (14), the wave number differences $\triangle\nu$ of these monochromatic radiation as follows:

$$\triangle\nu = \frac{W(m_1, m_2, m') - W(n_1, n_2, n')}{h} = (n_1, n_2, n') - (m_1, m_2, m') \quad (15)$$

where $$(n_1, n_2, n') = N\left(\frac{E(n_1, n_2, n')}{e}\right)^2 \left\{\frac{1}{(n_1+n_2+n')^2} + \frac{\alpha^2}{(n_1+n_2+n')^4}\left(\frac{E(n_1, n_2, n')}{e}\right)^2\left(\frac{1}{4} + \frac{n'}{n_1+n_2}\right)\right\} \quad (16)$$

Two terms on the right side of the formula (15) should represent the magnitude of the energy levels measured from the same standard state.

According to Broglie[2], Hertz[3], Duane and Patterson[4], there exist one, three, and five absorption edges in the regions of the K, L, and M series respectively, each one of these absorption edges, as is noticed by Duane[5], Smekal[6], and others, corresponds to one of the energy levels of the stationary orbits.

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1 Atombau u. Spektrallinen, 3 Aufl., 3 Kapital, s. 200.
2 C. R., **158**, 1493, (1914).
3 Z. S. f. Phys., **3**, 19, (1920).
4 Proc. Nat. Ac. Sc. Washington, Sept., (1920).
5 Proc. Nat. Ac. Sc. Washington, **6**, 477, (1920).
6 Z. S. f. Phys., **5**, 121, (1921).

Now, following the general designation, let K, L_1, L_2, L_3, M_1, M_2, M_3, &c., be respectively the stationary orbits counted from the inside of the atom, corresponding to the absorption edges in the regions of the K, L, M, Series. These are considered to the same as those denoted by the same symbols in the case of emission.

It is well known that there exist several pairs of lines in X-Ray spectra which are called " regular doublets ". If we mention these regular doublets in order of increasing wavelengths, we get for

the L_1 L_2 doublets: $K\alpha_1$-$K\alpha_2$, L_l-$L\eta$ $L\alpha_2$,-$L\beta_1$, $L\beta_6$-$L\gamma_5$, $L\beta_7$-$L\gamma_7$, $L\beta_5$-$L\gamma_6$,

the M_1 M_2 doublets: $L\alpha_1$,-$L\alpha_2$, $M\beta$-$M\alpha_2$,

the M_3 M_4 doublets: $K\beta_1$-$K\beta_3$, $L\beta_3$-$L\beta_1$,

the N_1 N_2 doublets: $M\alpha$-$M\alpha_2$,

the N_5 N_6 doublets: $K\gamma$-$K\beta_2$, $L\gamma_3$-$L\gamma_2$.

Among these regular doublets, let us restrict ourselves, for the present to the consideration of the L_1 L_2 doublets only.

With regard to these L_1 L_2 doublets, it has already been noticed by Sommerfeld that the following data should hold:

(a) The wavelength-differences between the components of the doublets remain always constant throughout all the atomic numbers of the elements.

(b) For each element the wave number-difference between the components of the L_1 L_2 doublets are not only equal to each other, but also equal to the wave number-differences between the absorption edges, L_1 and L_2.

(c) The 4th roots of the wave number-differences between the components of the regular doublets have always a linear relation to the atomic numbers of the elements.

Not only is the appearance of these doublets very similar to that of the hydrogen doublets, but there exists the following simple relation between the wave number-differences of these two kinds of doublets:

$$\Delta\nu_L\,(Z-3{\cdot}5)^4 \doteqdot \Delta\nu_H \qquad (17)$$

where $\Delta\nu_L$ and $\Delta\nu_H$ are the wave number differences between the components of the L_1 L_2 doublets and the hydrogen doublets respectively. What we have briefly stated above in the case of the L_1 L_2 doublets, generally holds with regard to the other regular doublets, viz.:

(i) The wavelength-differences between the components of a regular doublet remain nearly constant throughout all the elements.

(ii) For each element, the wave numbers-differences between the components of the regular doublets belonging to the same kind (e. g., the regular doublets $K\alpha_1$-$K\alpha_2$, L_l-$L\eta$, $L\alpha_2$-$L\beta_1$, &c., belonging to the L_1 L_2 doublets) are not only equal to each other, but also equal to the wave number-differences between the absorption edges corresponding to this

kind of regular doublets (e. g., the wave number-difference between the absorption edges L_1 and L_2 corresponding to the L_1 L_2 doublets are equal to those of the regular doublets belonging to the L_1 L_2 doublets for each element)

(iii) The 4th roots of the wave number-differences between the components of the regular doublets have always a linear relation to the atomic numbers of the elements.

Now modeling ourselves on Sommerfeld's idea, let us assume that the regular doublets in X-ray sqectra are generated, similarly to the hydrogen doublet, by the splitting of the lines due to the difference in the radial quantum numbers n' of the initial or final stationary orbits, corresponding to the same values of n_1+n_2+n' and n_2. That is, we suppose that the regular doublets are formed either by the falling of electrons from the same initial stationary orbit down to two different final stationary orbits specified above or by the falling from the two different initial stationary orbits specified above down to the same final stationary orbit.

With regard to the L_1 L_2 doublets, it is generally accepted that they are formed by the falling of the electrons from the initial stationary orbits L_1 and L_2 down to the same final stationary orbit (as in the case of the $K\alpha_1$-$K\alpha_2$ doublet), or from the same initial stationary orbit to the final stationary orbits L_1 and L_2 (as in the cases of the L_i-$L\mu$, $L\alpha_2$-$L\beta_1$, $L\beta_6$-$L\gamma_5$, $L\beta_7$-$L\gamma_7$, $L\beta_5$-$L\gamma_6$, doublets) respectively.

According to the view generally accepted, let us suppose that the sum of the three quatum numbers corresponding to the K, L, M, N, &c., orbits be respectively 1,2.3,4,&c. Then it is clear from the above conclusion, that the numerical values of n_1+n_2+n' corresponding to the L_1 and L_2 stationary orbits remain always equal to 2, while those of the radial quantum numbers are 1 and 0 respectively.

As to the choice of the quantum values among n_1, n_2, and n', we have omitted the case when $n_1=0$ by the intensity law which will be stated in the next chapter. Now, it is presumable that the effective nuclear charges of the stationary orbits, each one of which is situated near by the others, are equal. As the stationary orbits corresponding to the quantum numbers [1,0,1] and [2,0,0] satisfy the above condition we may put $E_{(1,0,1)} = E_{(2,0,0)} = (Z-\epsilon)e$ where ϵ is a certain correction term. Then the wave number-difference $\Delta\nu_L$ corresponding to this pair of quantum numbers will be obtained from (15) as written in (18)

$$\Delta\nu_L = (1,0,1) - (2,0,0)$$

$$\doteqdot N\left[\frac{1}{2^2}\left\{\left(\frac{E_{(1,0,1)}}{e}\right)^2-\left(\frac{E_{(2,0,0)}}{e}\right)^2\right\}+\frac{\alpha^2}{2^4}\left\{\left(\frac{E_{(1,0,0)}}{e}\right)^4\right.\right.$$

$$\left.\left.-\left(\frac{E_{(2,0,0)}}{e}\right)^4\right\}\frac{1}{4}+\frac{\alpha^2}{2^4}\left(\frac{E_{(1,0,1)}}{e}\right)^4\right]=\frac{N\alpha^2}{2^4}(Z-\epsilon)^4$$

$$=\Delta\nu_H(Z-\epsilon)^4=L_2-L_1 \qquad (18)$$

As this equation represents the relation which must be satisfied by a regular doublet, we have equated the value, thus calculated, to L_2—L_1. Consequently we may assign the quantum numbers [1,0,1] and [2,0,0] to L_1 and L_2 respectively.

The above expression (18) which represents the wave number-difference between the components of the L_1 L_2 doublets. is the same as the corresponding expression in Sommerfeld's paper[1]. Accordingly, if we substitute $\epsilon = 3{\cdot}5$ as does Sommerfeld, the expression (17) previously given is reduced from (18)

What we have illustrated above concerning the L_1 L_2 doublets, can also be explained to hold, with regard to the other regular doublets, from our preceding idea of the 3 quantum numbers. Thus, the part concerning the elliptic orbits of Sommerfeld's theory is included as the special case in our foregoing considerations of the 3 quantum numbers. Moreover, the difficulty of his theory with regard to the number of the absorption edges is removed in the present consideration by the abolition of limitation of all the electronic orbits to the coplaner orbits.

§ 4. *On the Selection Principle of X-Ray Spectra.*

As has already been stated, there are one, three, and five absorption edges in the regions of the K, L, M series respectively, and these absorption edges correspond to the energy levels of the stationary orbits represented by the same alpabetical symbols. It may, therefore, be expected that the wave number of each line in X-ray spectra should be equal to the wave number-difference between two absorption edges corresponding to the initial and final stationary orbits.

In point of fact, by adequately combining the wave numbers of the lines and those of the absorption edges, Coster[2], Sommerfeld[3] and others determined the initial and final stationary orbits of electrons to produce the X-ray spectra as shown in Table 2.

From the following Table 2, it is clear that the wave number of every line can be equated to the wave number-differences between two absorp-

1. Atombau u. Spektrallinien, 3 aufl., s. 608.
2. Z. f. Phys., 6, s. 188, (1921).
3. Atombau u. Spektrallinien, 3 Aufl., s. 635.

Table 2.

The initial and final stationary Orbits of Electrons in X-Ray Radiations

$K\alpha_3$; $L_3 \longrightarrow K$	$L\gamma_2$; $N_6 \rightarrow L_3$	$L\beta_2$; $N_3 \rightarrow L_1$
$K\alpha_2$; $L_2 \longrightarrow K$	$L\gamma_3$; $N_5 \rightarrow L_3$	$L\gamma_1$; $N_4 \rightarrow L_2$
$K\alpha_1$; $L_1 \longrightarrow K$	Ll; $M_5 \rightarrow L_1$	$M\alpha_1$; $N_1 \rightarrow M_1$
$K\beta_3$; $M_4 \longrightarrow K$	$L\eta$; $M_5 \rightarrow L_2$	$M\alpha_2$; $N_2 \rightarrow M_2$
$K\beta_1$; $M_3 \longrightarrow K$	$L\alpha_2$; $M_2 \rightarrow L_1$	$M\beta$; $N_2 \rightarrow M_2$
$K\beta_2$; $N_6 \longrightarrow K$	$L\alpha_1$; $M_1 \rightarrow L_1$	$M\gamma$; $N_3 \rightarrow M_3$
$K\gamma$; $N_5 \longrightarrow K$	$L\beta_1$; $M_2 \rightarrow L_2$	$M\delta$; $N_4 \rightarrow M_3$
$L\beta_4$; $M_4 \longrightarrow L_3$	$L\beta_6$; $N_7 \rightarrow L_1$	
$L\beta_3$; $M_3 \longrightarrow L_3$	$L\gamma_5$; $N_1 \rightarrow L_2$	

tion edges; but, the inverse statement does not hold and there are many missing lines corresponding to some pairs of two absorption edges.

In this chapter we shall, therefore, limit ourselves to the explanation of such a selective transition of electrons in an atom, from our consideration of taking the three different kinds of quantum numbers.

Now, let the quantum numbers of the initial and the final stationary orbits be $[m_1, m_2, m']$ and $[n_1, n_2, n']$ respectively. Then, from the energy law, we have obviously, for every actual passage of the electron, associated with radiation.

$$m_1 + m_2 + m' > n_1 + n_2 + n' \qquad (19)$$

If we assume that Sommerfeld's first law of quantum inequalities holds also good in the present case, we can suppose that under the normal state only such passages as are restricted by the following relations are possible.

$$m_1 \geqq n_1 \qquad m_2 \geqq n_2 \qquad m' \geqq n' \qquad (20)$$

Moreover, we shall assume that even if radiations which do not follow the above restriction (20) occur, these exceptions will be of small intensity.

As the measure of the possibility P of the occurrence of an electron on the stationary orbits corresponding to $[n_1, n_2, n']$, let us consider, following Sommerfeld's proposition,

$$P = \frac{n_1}{n_1 + n'} \qquad (21)$$

Then from the above expression (21), it can easily be seen that the numerical value of P corresponding to a stationary orbit on the longitudinal plane of the atom and that corresponding to a rectilinear orbit passing through the nucleus of the atom are equal to zero; while that corresponding to a circular orbit remains always 1. In the other cases,

Table 3.

The possible Quantum Numbers of the stationary Orbits.

Name of the Series and their whole Quantum Numbers	Case $n_2=0$			Case $n_2=1$			Case $n_2=2$			Case $n_2=3$			Case $n_2=4$		
	Quantum Numbers n_1,n_2,n'	Relative Int. P	Name of the Energy Levels	Quantum Numbers n_1,n_2,n'	Relative Int. P	Name of the Energy Levels	Quantum Numbers n_1,n_2,n'	Relative Int. P	Name of the Energy Levels	Quantum Numbers n_1,n_2,n'	Relative Int. P	Name of the Energy Levels	Quantum Numbers n_1,n_2,n'	Relative Int. P	Name of the Energy Levels
K Series $n_1+n_2+n'=1$	(1,0,0)	1	K												
L Series $n_1+n_2+n'=2$	(2,0,0)	1	L_1	(1,1,0)	1	L_3									
	(1,0,1)	$\frac{1}{2}$	L_2												
M Series $n_1+n_2+n'=3$	(3,0,0)	1	M_1	(2,1,0)	1	M_3	(1,2,0)	1	M_5						
	(2,0,1)	$\frac{2}{3}$	M_2	(1,1,1)	$\frac{1}{2}$	M_4									
	(1,0,2)	$\frac{1}{3}$													
N Series $n_1+n_2+n'=4$	(4,0,0)	1	N_1	(3,1,0)	1	N_3	(2,2,0)	1	N_5	(1,3,0)	1	N_7			
	(3,0,1)	$\frac{3}{4}$	N_2	(2,1,1)	$\frac{2}{3}$	N_4	(1,2,1)	$\frac{1}{2}$	N_6						
	(2,0,2)	$\frac{2}{4}$		(1,1,2)	$\frac{1}{3}$										
	(1,0,3)	$\frac{1}{4}$													
O Series $n_1+n_2+n'=5$	(5,0,0)	1		(4,1,0)	1		(3,2,0)	1	O_1	(2,3,0)	1	O′	(1,4,0)	1	
	(4,0,1)	$\frac{4}{5}$		(3,1,1)	$\frac{3}{4}$		(2,2,1)	$\frac{2}{3}$	O_2	(1,3,1)	$\frac{1}{2}$				
	(3,0,2)	$\frac{3}{5}$		(2,1,2)	$\frac{2}{4}$		(1,2,2)	$\frac{1}{3}$	O_3						
	(2,0,3)	$\frac{2}{5}$		(1,1,3)	$\frac{1}{4}$										
	(1,0,4)	$\frac{1}{5}$													

P always takes numerical values between o and 1.

It is generally known that the sum of the three quantum unmbers n_1+n_2+n' of the K, L, M, N, and O orbits are 1, 2, 3, 4 and 5, respectively. By keeping constant the total sum of n_1, n_2, n', and giving various values to every one of these quantum numbers we get the combinations given in Table 3.

From these quantum numbers given in Table 3, the numerical values of P can be derived as the consequence of the foregoing expression (21).

As has already been stated, every one of these numerical values of P is the measure of the possibility of occurrence of an electron in the corresponding stationary orbit. Thus, to a larger numerical value of P of a stationary orbit, there corresponds an absorption edge of the larger intensity. In the above Table 3, the cases when $n_1=0$ are excluded, because the numerical values of P remains always o in such cases.

Now, let us consider what distribution of the spectrum lines should naturally be expected, as the necessary consequence of our foregoing arguments which are based on the assumption of three kinds of quantum numbers. To begin with, however, it would be advisable to limit ourselves to the discussion of the stationary orbits up to the N region. As regards the stationary orbits in the O region there are some interesting points, and to these points we shall come back later in Chapter 5.

Now, suppose that out of all possible stationary orbits only those which correspond to the numerical values of P larger than $\frac{1}{2}$, are responsible for X-ray phenomena observed up to the present time.

The quantum numbers corresponding to such stationary orbits are underlined in Table 3. (Notwithstanding, both quantum numbers [2, 0, 2] and [1, 2, 1] of the stationary orbits in the N series correspond to the same $P=\frac{1}{2}$, but the former only is excluded from underlining. This can be explained by the fact that the stationary orbit of the quantum numbers [2, 0, 2] only is responsible — as will be stated later — for the radiations of the longer wavelengths as in the M and N series.)

Then, the stationary orbits of the following quantum numbers which are underlined, should be detectable in the region of each series: i. e., we have

in the K series: [1, 0, 0]
in the L series: [1, 0, 1]⟷[2, 0, 0] [1, 1, 0]
in the M series; [2, 0, 1]⟷[3, 0, 0] [1, 1, 1]⟷[2, 1, 0] [1, 2, 0]
in the N series; [3, 0, 1]⟷[4, 0, 0] [2, 1, 1]⟷[3. 1, 0]
[1, 2, 1]⟷[2, 2, 0] [1, 3, 0]

Consequently, there are 1, 3, 5, and 7 stationary orbits in the regions of the K, L, M, and N series respectively.

The stationary orbits corresponding to the equal radial quantum numbers n_2 and the sum of the three quantum numbers n_1 n_2 n', are connected by the symbol←→in the above expression. Such orbits should, according to our foregoing consideration, be responsible for the formation of regular doublets. Thus we arrive, theoretically, at the conclusion — a conclusion which agrees well with the experiments — that there should exist 1, 3, 5, and 7 energy levels in the regions of the K, L, M, and N series respectively: moreover, there should exist 1, 2, and 3 regular doublets in the spectra belonging to the L, M, and N series repectively.

Thus having confirmed the above, it may be well to discuss the selection principle in X-ray spectra, as the furtherance of our foregoing argument. Let us first consider the effect due to the repulsion of the inner electrons in the same atom, on a revolving electron. Now, suppose that this effect is larger, when the angle between the equatorial plane and the ecliptic plane of this electron is smaller: i. e., to the larger spatial quantum number n_2, there should correspond the larger effective nuclear charge.

It is quite obvious that, as the consequence of the foregoing expression (15), the wave number-difference between the components of a regular doublet is proportional to the 4th power of the numerical value of the effective nuclear charge. Thus, among a number of the regular doublets belonging to the same series, the one corresponding to the larger spatial quantum number should be of the larger wave number difference.

Consequently, it would be legitimate to consider

$$\left.\begin{aligned} &\Delta\nu_{M_{(1.1.1)}-M_{(2.1.0)}} > \Delta\nu_{M_{(2,0,1)}-M_{(3,0,0)}} \\ &\Delta\nu_{N_{(1,2,1)}-N_{(2,2,0)}} > \Delta\nu_{N_{(2,1,1)}-N_{(3,1,0)}} \quad \Delta > \nu_{N_{(3,0,1)}-N_{(4,0,0)}} \end{aligned}\right\} (22)$$

where $\Delta\nu_{X_{(k_1,k_2,k')}-X_{(l_1,k_2,l')}}$ represents the wave number-difference of the regular doublet corresponding to the two energy levels characterized by $X_{(k_1,k_2,k')}$ and $X_{(l_1,k_2,l')}$ respectively.

With regard to the regular doublets, the following conclution are well known as the outcome of the experiments:—

(1) The wave number-difference between the energy levels L_1 and L_2 in the L series, M_1 and M_2, M_3 and M_4 in the M series, N_1 and N_2, N_3 and N_4, N_5 and N_6 in the N series are equal to the wave number-differences of the corresponding regular doublets in the same series.

(2) These regular doublets in each series can be arranged in order

of decreasing wave number-differences as follows:
for the L series; L_1 L_2 doublet,
for the M series; M_3 M_4 doublet, M_1 M_2 doublet,
for the N series; N_4 N_6 doubelt, N_3 N_4 doublet, N_1 N_2 doublet.

Now, from our foregoing expression (22), the quantum numbers corresponding to each one of the energy levels can be assigned. This assignment is so made that it agrees with the experimental results above mentioned, referring to the order of the wave number-differences of the regular doublets. According to this assignment, there should exist a correspondence between the quantum numbers and the energy levels as shown in Table 3:

Thus, referring to the planes of the orbits, we can affirm the following propositions:—

(1) The electron can move from a certain outer stationary orbit to the next one as from L to K and M to L, without changing its spatial quantum uumber, or by loosing it in even number.

(2) In every radiation caused by the transition of electrons from a certain outer orbit to the inner one passing through some intermediate orbits as from M to K, from N to L, and from O to K, the spatial quantum numbers of the initial and final orbits are not equal; the electron loses its spatial quantum number by 1 or by an old number every time when it passes through one of the intermediate orbits.

These propositions give physical basis to the "transition law" previously deduced by the present writer[1], as well as to Coster's a-b law[2] in certain respects. The only defficulty in our conclusions is that there is an exception with regard to a line $K\alpha_3$ observed by Duane and Stenstrom[3]. But this line is very feeble and has only been mentioned in Duane's paper. Thus the exceptions to our propositions, if any, should occur very infrequently and be of very small intensity.

Owing to our propositions mentioned above, the ecliptic plane of revolving electron tends to the equatorial plane, on every occasion when the transition takes place by passing through some intermediate orbits. This may probably be due to the magnetic field caused by the majority of electrons revolving in the equatorial plane.

Previously, we omitted the energy level [2, 0, 2] in our foregoing discussion, while the energy level [1, 2, 1] was taken into account in spite of the fact that the relative intensities in both cases are the same and equal

1 Proc. Roy. Soc., **105**, 59, (1924).
2 Z. f. Phys., **6**, 202, (1921).
3 Phys. Rev., **15**, 328, (1920).

to $\frac{1}{2}$.

The reason for this may be explained as follows :—

As the energy level [2, 0, 2] corresponds to the numerical value 0 of the spatial quantum number n_2, it follows from the preceding propositions that the radiations concerned in this energy level should neither belong to the K nor to the L series. They should belong to the M or the N series. In such regions of X-ray spectra, the lines are hardly detectable. The lines observed in these regions are all of a stronger intensity. Consequently, it is inconceivable that the lines which are conserned in the stationary orbits of such a weak intensity as $P=\frac{1}{2}$, can have been observed up to the present time.

On the other hand, the energy level [1, 2, 1] corresponds to the numerical value 2 of the spatial quantum number n_2. There should exist some lines in the K and the L series, which are formed by the electrons having [1, 2, 1] at their initial orbit. It should, therefore, have some effect upon the experimental results, even tho the relative intensity P be $\frac{1}{2}$.

This is the reason, why the enegry level [1, 2, 1] was only mentioned in our previous discussion.

In a similar way, we can explain the fact that there do not exist any detectable energy levels in the O series, when $n_2=0$, and $n_2=1$.

Not only those stated above, with regard to the O orbit, the following can be presupposed fron our second proposition :—

The lines produced by the electrons falling from the O orbit down to the L orbit, the numerical value of n_2 of the initial orbit should be 2 (in the case when the final orbit is L_1 or L_2), or 3 (in the case when the final orbit is L_3), while if the lines belong to the K series, the spatial quantum number n_2 of the initial O orbit should be 3.

§ 5. *On the O-Triplets in X-Ray Spectra belonging to the L-Series.*

Coster noticed that besides the regular doublets, there exist some lines in the L series between which the wavelength differences remain the same throughout all the elements. Table 4 shows such differences of wavelengths.

From Table 4, it is easy to see that the differences of the wavelength between $L_{\beta_7}-L_{\beta_5}$ and $L_{\beta_8}-L_{\beta_7}$ etc., remain constant throughout the whole element. Table 5 shows the wavelength differences between $L_{\beta_7}-L_{\beta_5}$, $L_{\beta_8}-L_{\beta_7}$, and $L_{\gamma_6}-L_{\gamma_7}$.

Generally, let us consider the case when an electron has fallen down from one of the initial stationary orbits of the quantum number $M=m_1+$

m_2+m', to one of the final stationary orbits of the quantum number $N=n_1+n_2+n'$, and it suddenly radiates out that defference of energy in the form of a mono-chromatic wave. In such a case, if we neglect the effect due to the repulsion of the fellow elections, the wave number ν of the mono-chromatic wave should be expressed by

$$\nu=(n_1, n_2, n',)-(m_1, m_2, m',) \qquad (23)$$

where n_1, n_2, n', are the azimal, spatial, and radial quantum numbers of the final orbits and m_1, m_2, m' are those of the initial as stated in § 1.

The stationary orbits in the equatorial plane of the quantum number

Table 4.

The Constant Differences of the Wavelengths (λ in 10^{-11} cm)

Atomic Number	$\beta_2-\beta_5$	$\gamma_1-\gamma_6$	γ_2-3	$\beta_4-\beta_3$	$\beta_2-\beta_8$	$\beta_2-\beta_7$
73 Ta	30·4	24·71	5·8	38·9	7·5	21·0
74 W	29·41	23·53	6·19	38·74	6·5	21·11
76 Os	28·38	——	——	37·8	—	——
77 Ir	29·87	24·8	7·0	38·5	6·2	——
78 Pt	29·40	23·75	6·1	40·3	6·7	21·10
79 Au	29·55	23·1	5·57	——	6·8	21·25
81 Tl	29·56	23·59	6·8	39·3	—	19·9
82 Pb	30·38	23·38	4·5	38·67	6·4	20·9
83 Bi	30·63	23·25	5·5	39·7	—	——
90 Th	28·49	20·93	——	36·9	—	——
92 U	28·55	20·23	7·4	37·0	—	19·68

Table 5.

Atomic Number	Differences of the wavelengths		Differences of the wavenumber		Ratio	Differences of wavelengths.	Differences of wavenumber
	$\beta_7-\beta_5$	$\beta_3-\beta_7$	$\nu\beta_5-\nu\beta_7$	$\nu\beta_7-\nu\beta_3$	$\gamma\beta_5-\gamma\beta_7/\gamma\beta_7-\gamma\beta_3$	$\gamma_7-\gamma_6$	$\gamma_6-\gamma_7$
73 Ta	9·4	13·8	5·35	7·70	3 : 4·3		
74 W	8·3	14·6	5·11	9·15	3 : 5·3	6·8	4·90
76 Os	—	——	——	——	——		
77 Ir	—	——	——	——	——		
78 Pt	8·4	14·3	6·64	11·03	3 : 5·1		
79 Au	8·3	14·4	6·93	11·83	3 : 5·1		
81 Tl	9·7	——	8·83	(13·92)	3 : 4·9		
82 Pb	9·48	14·5	9·51	14·19	3 : 4·5		
83 Bi	—	——	——	——	——		
90 Th	—	——	——	——	——		
92 U	11·87	——	20·29	——	——		

N consist of N elliptic orbits of defferent ellipticites. With respect to the stationary orbits in the planes characterized by $n_2=2$ of the quantum number M the foregoing consideration should, also holds and they consist of M-2 different elliptic orbits.

Now, suppose that the quantum numbers of the initial orbits M be 5 and that of the final orbits N be 2, and the final orbits are situated in the equatorial plane. Then the initial orbits should, according to our foregoing proposition in § 4, be situated in the planes characterized by $n_2=2$.

For the sake of convenience we shall call these orbits in the order of their eccentricities as 1st. final orbit, 2nd. final orbit and 1st. initial orbit, 2nd initial orbit, 3rd. initial orbit, &c. respectively.

In this case quantun numbers of the initial and final orbits are expressed by

$$\left.\begin{aligned} N &= n_1+n_2+n'=2 \\ M &= m_1+m_2+m'=5 \end{aligned}\right\} \quad \cdots\cdots (24)$$

The radiations are emitted when an electron passes from one of the initial orbits to one of the final orbits. Therefore we should have two sets of triplets; one caused by the falling down of an electron from 3 different initial orbits to one of the final orbits, and the other is formed by combining the 3 initial orbits with the other of the final orbits. Thus the wave numbers of the components of one of the triplets are.

$$\left.\begin{aligned} \nu_{1-1} &= (2,0,0)-(3,2,0) \\ \nu_{1-2} &= (2,0,0)-(2,2,1) \\ \nu_{1-3} &= (2,0,0)-(1,2,2) \end{aligned}\right\} \quad \cdots\cdots (25)$$

and those of the other set of triplets are.

$$\left.\begin{aligned} \nu_{2-1} &= (1,0,1)-(3,2,0) \\ \nu_{2-2} &= (1,0,1)-(2,2,1) \\ \nu_{2-3} &= (1,0,1)-(1,2,2) \end{aligned}\right\} \quad \cdots\cdots (26)$$

where ν s—t means the wave number of the radiation emitted by the transition of an electron from the t^{th} initial orbit to the s^{th} final orbit.

It will easily be seen from (25) and (26) that the wave number-differences between any two corresponding numbers of the two sets of triplets must be the same, as shown by the following relations.

$$\nu_{2-1}-\nu_{1-1}\equiv\nu_{2-2}-\nu_{1-2}\equiv\nu_{2-3}-\nu_{1-3}\equiv(1,0,1)-(2,0,0) \cdots\cdots (27)$$

By (25) and (26) the wave number differences between two successive components of a triplet should be expressed by

$$\left.\begin{aligned} \triangle\nu_1 &= \nu_{1-2}-\nu_{1-1}=\nu_{2-2}-\nu_{2-1}=(2,2,1)-(3,2,0) \\ \triangle\nu_2 &= \nu_{1-3}-\nu_{1-2}=\nu_{2-3}-\nu_{2-2}=(1,2,2)-(2,2,1) \end{aligned}\right\} \quad \cdots\cdots (28)$$

The above propositions can be applied to the case of x-ray radia-

tion by replacing the nuclear charge $\frac{E}{e}$ in the formulae (27) and (28) with the proper effective nuclear charges.

If we consider the K. L. M. N. O. P. ..... orbits as the stable orbits in an atom, then the K. L. M. N. O. P ..... terms should have the quantum numbers 1, 2, 3, 4, 5, 6..... respectively. Now let us assume $L\beta_5$ to be generated by the falling down of an electron from one of the O orbits to one of the L orbits, then this line should be a component of one of the triplets. It can naturally be supposed that $L\gamma_6$ line is also a component corresponding to $L\beta_5$ of the other triplet, because $L\gamma_6$ forms an L doublet with $L\beta_5$.

Let o be the correction due to the effect of the other fellow electrons in the atom, to be applied to the nuclear charge for O term; then (Z-o)e should be the effective nuclear charge for this term. Thus for the triplet due to the O term, the wave number differences between them can be obtained by putting the total effective nuclear charge E equal to (Z-o)e in (28)

$$\left.\begin{aligned} \triangle \nu_1 &\fallingdotseq \frac{N\alpha^2}{5^4}\,\frac{1}{4}(Z-o)^4 \\ \triangle \nu_2 &\fallingdotseq \frac{N\alpha^2}{5^4}\,\frac{5}{12}(Z-o)^4 \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (29)$$

Therefore

$$\triangle \nu_1 : \triangle \nu_2 \fallingdotseq 3 : 5 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (30)$$

The differences of the wave numbers between the lines and the ratio between them are shown in Table 5. Actually it is very remarkable that for all the elements examined the ratio of the wave number differences between $L\beta_5 - L\beta_7$, $L\beta_7 - L\beta_8$ remain always the same and equal to $\triangle \nu_1 : \triangle \nu_2 = 3 : 5$ as shown in (30) within the limit of experimental errors.

In the case of tungsten, the line $L\gamma_6$ which forms a doublet with $L\beta_5$ accompanies a feeble line $L\gamma_7$, and the difference of the wave numbers between them is equal to that between $L\beta_5$ and $L\beta_7$, within the limit of experimental errors.

Thus, it seems to be legitimate to consider that the lines $L\beta_5$, $L\beta_7$ $L\beta_8$ belong to one of the two sets of triplets, and that $L\gamma_6$ and $L\gamma_7$ belong to the other set of triplets, and the wave numbers of these lines will be represented by.

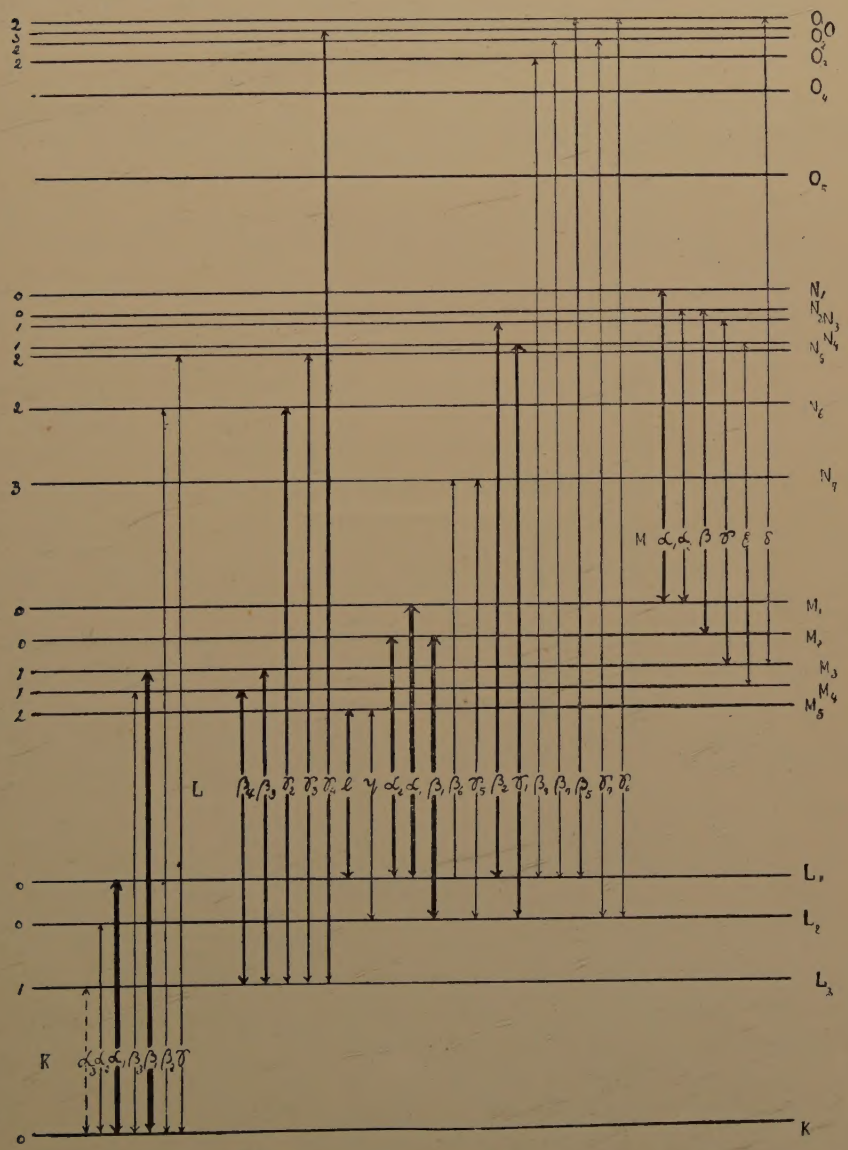
$$\left.\begin{aligned} L\beta_5 \quad & \nu = L_1 - O_1 \\ L\beta_7 \quad & \nu = L_1 - O_2 \end{aligned}\right\}$$

$$\left.\begin{array}{ll} L\beta_3 & \nu = L_1 - O_3 \\ L\gamma_6 & \nu = L_2 - O_1 \\ L\gamma_7 & \nu = L_2 - O_2 \end{array}\right\} \quad \cdots\cdots\cdots\

The numerals on the left side of Fig. 2, represent the numerical values of n_2 of the energy levels in this figure.

In conclusion the writer's sincere thankes are due to Professor T. Mizuno, Professor K. Kimura, Professor M. Ishino, Professor K. Tamaki, and Professor U. Yoshida, for their kindly interest in this investigation.

Fig. 2.



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